Applied Surface Science
Room 101B - Session AS-WeA

Multiple Technique Approaches for Real-World Industrial Problem Solving

Moderators: Kateryna Artyushkova, University of New Mexico, Xia Dong, Eli Lilly and Company

2:20pm **AS-WeA1 Integrated XPS/ Raman Spectroscopy for Comprehensive Structural, Molecular and Chemical Surface Analysis***, **Christopher Deeks**, P. Mack, T.S. Nunney, J.P.W. Treacy, M. Meyer, N. Hibbard,* Thermo Fisher Scientific, UK

Advanced materials present ever increasing challenges to the analytical scientist. Composite materials built from nanostructures or ultra-thin films, often with complex chemistries present, are now required in a broad range of applications, and achieving full characterization is rarely managed using only one analysis method. To maintain confidence in the results from the utilization of several different methods, it is advantageous to be able to perform experiments on the same platform. Ideally, this should be without having to move the sample, removing the need for additional registration or processing to ensure that the data is being collected from the same position.

Often in surface analysis many related techniques are integrated onto the same system. These can include such practices as Ultraviolet Photoelectron Spectroscopy (UPS) for valence band and work function measurements. Ion Scattering Spectroscopy (ISS) is often used to give much more elemental surface information compared to XPS alone. Reflected Electron Energy Loss Spectroscopy (REELS) can also give information on hydrogen in samples which cannot be detected by any of the previously named techniques, allowing full elemental analysis of samples with these combined.

An integrated system that has a Raman spectrometer with a micro-focused, monochromated XPS system can be used for even further analysis. The focal points are aligned such that data can be acquired from the same point simultaneously, and that the sizes of the analysis areas are comparable in size. This combined approach is particularly powerful when analyzing carbon nanomaterials. Chemical modifications of the material can be easily determined and quantified with XPS, and Raman offers a fast way of determining the quality and conformity of the material. Vibrational structure can also give more precise chemical information in some cases. The greater depth of field of the Raman spectrometer also offers bulk information to complement the surface sensitive XPS data.

In this presentation we will discuss the strengths of this combined, in-situ approach to surface analysis, illustrated with examples from a range of applications including carbon nanomaterials, microelectronics and geology.

2:40pm **AS-WeA2 Extended Molecular Identification with TOF-SIMS Imaging MS/MS***, **John Hammond**, G.L. Fisher, S.R. Bryan,* Physical Electronics*; S. Iida, T. Miyayama,* ULVAC-PHI, Japan

TOF-SIMS has become widely accepted as the most powerful spectroscopy and imaging surface analysis tool for organic and polymer samples based on the capabilities of 2 nm surface sensitivity and 100 nm spatial resolution. For most polymer additives as well as lipids, disease markers and fatty acids on biological tissue samples, the molecular ions have masses up to m/z 1000. At this higher mass range, traditional TOF-SIMS lacks the mass resolution and mass accuracy to uniquely identify the detected ions. A new TOF-SIMS instrument combining, in parallel, imaging MS and imaging MS/MS provides the capability to provide a multi-technique approach to real world problem solving with extended molecular identification of higher mass ions [1].

A series of saturated and unsaturated fatty acid standards as well anti-oxidant polymer additives were analyzed with a PHI *nanoTOF* II TOF-SIMS Parallel Imaging MS/MS. The MS/MS spectra were generated with a 1 daulton precursor selection window followed by 1.5 keV collision-induced dissociation (CID). The MS^1 and MS^2 parallel imaging of polymer surfaces with a mixture of polymer additives were obtained with a raster scanned Bi_3^+ ion source with a sub-micron spatial resolution

The structural elucidation of the fatty acid CID MS/MS spectra can be interpreted by charge-remote fragmentation [2]. The location of unsaturated bonds in the fatty acids can be defined from these spectra. The complex structures of the anti-oxidants can be easily identified with the high energy CID MS/MS. Using the high signal/background of the MS^2 images, bunched or unbunched imaging with the Bi_3^+ ion source can produce sub-micron spatial resolution with unique molecular identification of additives on the polymer films. These results also point to a broader utility of this technique for biological tissue imaging.

4. References

[1] P.E. Larson, J.S. Hammond, R.M.A. Heeren, G.L. Fisher, *Method and Apparatus to Provide Parallel Acquisition of MS/MS Data*, U.S. Patent 20150090874, 2015.

[2] M. L. Gross,, Int. J. Mass Spectrom., 200 (2000) 611

3:00pm **AS-WeA3 Practical Aspects of Multiple Technique Problem-Solving: Making it Work***, **Kathryn Lloyd**,* DuPont Corporate Center for Analytical Sciences **INVITED**

Although there do exist types of problems or research support for which one analytical technique is sufficient to provide useful guidance or an answer, it is more the norm that multiple analytical techniques are required to address technical problems involving coatings, layered structures, and other industrial materials. In fact, basing action (e.g., a change in manufacturing process) on data from a single analytical technique -- especially a surface-specific technique – would not be advisable in most cases.

Some technique combinations seem intuitive – for example, combining the high-lateral-resolution detail from electron microscopy with the higher level of chemical information available from either secondary ion mapping (ToF-SIMS) or Raman microprobe analysis. However, there are still challenges with sample preparation, data acquisition from the same area, and data integration that need to be addressed.

Other technique combinations arise from the business need – for example, finding a combination of techniques that both describe the chemistry and correlate with end-use performance. This usually involves combining a vacuum-based technique with an ambient or "macroscopic" technique such as contact angle, porosity, or friction measurements.

As most practitioners know, the surface specificity of XPS and ToF-SIMS can be both an advantage and a disadvantage. In this regard, the introduction of GCIB (Gas Cluster Ion Beam) sources has opened up new opportunities for multiple-technique problem-solving.

This talk will present some experiences and examples that provide a flavor of multiple-technique problem-solving in an industrial environment.

4:20pm **AS-WeA7 Adhesion Aspects of Polymeric Methylene Diphenyl Diisocyanate on Different Steel Surfaces by XPS and ToF-SIMS***, **Jorge Bañuls Ciscar**, M.L. Abel, J.F. Watts,* University of Surrey, UK

Polymeric methyl diphenyl diisocyanate (p-MDI) is a versatile isocyanate commonly used in coatings and adhesives applications because of its excellent mechanical properties. In this work, we are aiming to understand the chemistry involved at the interface between p-MDI and a specific stainless steel as a result of different processing parameters. This steel has distinct surface properties. On one side the surface has been ground and the composition is mostly iron oxide (Fe_2O_3) whereas on the other side the steel has a mill-finished surface and the composition is predominantly chromium oxide (Cr_2O_3). Therefore, in our system of interest, the stainless steel has different physical and chemical properties on each side. As such, understanding the adhesion aspects of p-MDI on each side could lead to an improvement of its use in many steel applications.

Preliminary work using XPS and ToF-SIMS has shown an interaction between nitrogen and chromium oxide at the interface. A low binding energy peak (~397 eV) was identified in the N1s high resolution XPS spectrum. This peak represents nitrogen atoms which have a higher electronic density as a result of the electron withdrawing effect of the MDI on the metal substrate. Additionally, peaks of characteristic fragments of N-Cr interaction were found in the ToF-SIMS spectra. This will form the basis of further work to determine the exact chemistry involved in such interfacial regions.

4:40pm **AS-WeA8 Migration of Erucamide in Polyethylene Films***, **Michaeleen Pacholski**, R. Sharma, J. Ngunjiri, K. Laughlin, M. Kapur, V. Kalihari,* The Dow Chemical Company

Polyolefins are often formulated with additives to provide stability and processability depending on their end use. Reduction of coefficient of friction (COF) for polyolefin films is a critical property. A common additive for COF reduction is erucamide. Films made using this fatty amide are known to have diminished COF performance when exposed to elevated temperatures that might be found in hot trucks or warehouses. Characterization of these materials during and after thermal aging can provide useful understanding in deterioration of film performance. Here we use a multitechnique approach to characterize the surface chemistry and morphology of this relatively simple, yet common, system of polyethylene and erucamide.

5:00pm **AS-WeA9 Probing the Impact of Process and Materials Variability of Medical Device Components with Surface Characterization***, **Jeffrey Fenton**, L. Nygren, B. Tischendorf, R. Jahnke, J. Heffelfinger,* Medtronic plc

Since the first pacemaker implant in 1958, engineering and medical advances have greatly improved device capabilities and patient outcomes. Advances in materials chemistry have increased the need for deep understanding of process-material interactions and their role in device or component longevity. This presentation will focus on the utilization of X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) on processes related to two device components, feedthroughs and printed wire boards, as a means to improve processing conditions, expand processing boundaries, and understand failure modes.

In pacemakers or like devices, feedthroughs are evaluated using various electrical tests to determine the insulation resistance which is typically in the Megaohm or Gigaohm range. XPS and SEM analysis will be shown to aid in the determination of yield loss root cause by identifying sources of foreign materials. For example, fibers from clothing may deposit onto the insulator and graphitize during high temperature processes. The graphitized materials may then provide a pathway for conductivity during electrical testing. Compositional and morphological identification with SEM allows for root cause identification and elimination of those yield losses.

Laser soldering, which is relatively new to the industry, is utilized in new Medtronic products. During the laser soldering process localized heat results in a different wetting dynamic from the conventional furnace reflow. The laser soldering process may be used after preceding thermal exposure in the upstream processes resulting in changes to the surface condition of the soldering pads. The surface chemistry may change during thermal exposure which may cause reduced wettability and create one of the biggest challenges during the process development to overcome. XPS, SEM and XRF (x-ray fluorescence) methods provide key insight on the inter-diffusion between the metallization layers on the PBW and migration to the surface species that can limit pad solderability. The main outcome of the analysis was establishing design rules for the PWB plating, including metallization materials and layer thickness in multilayer metallization.

5:20pm **AS-WeA10 Multi-technique Characterization of PtNi Extended Surface Catalysts for Improvement of Electrocatalytic Activity and Durability***, S. Shulda, C. Ngo,* Colorado School of Mines*; S. Alia,* National Renewable Energy Laboratory*; J. Nelson Weker,* SLAC National Accelerator Laboratory*; B. Pivovar,* National Renewable Energy Laboratory*; **Svitlana Pylypenko**,* Colorado School of Mines

Transition metal nanowires are emerging as an effective structure for various heterogeneous catalysis applications. Metal and metal oxide nanowires have demonstrated high activity for the oxidative coupling of methane into higher value products, hydrogenation of aromatic compounds, and water splitting, among others. Of particular interest is the application of platinum-nickel and platinum-cobalt nanowires as oxygen reduction catalysts in polymer electrolyte membrane fuel cells (PEMFCs) as they have shown activities that significantly surpass the current state of the art Pt nanoparticles supported on high surface are carbon and are considered a promising alternative. The activity and durability of Pt nanowires is dependent on both the surface and bulk properties, which continuously evolve during different steps of the synthesis, electrode preparation, and fuel cells operation, making a multi-technique analysis approach necessary.

High surface area platinum nickel (PtNi) nanowires have been synthesized via spontaneous galvanic displacement. Various post-processing treatments were applied altering the chemistry and structure of the nanowires to improve their activity and durability. This work focuses on the analysis of the surface and bulk composition and structure and their evolution with various treatments. X-ray photon spectroscopy (XPS), energy dispersive x-ray spectroscopy (EDS) via transmission electron spectroscopy (TEM), x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectroscopies, and transmission x-ray microscopy (TXM) were utilized. All of the processing treatments altered the surface chemistry and in some instances the morphology of the nanowires, with some treatments resulting in increased activity and durability while others being detrimental to the performance. The extensive characterization of the nanowires pre- and post-processing provided a robust understanding of each treatments effect on the nanowires and guided the optimization of the post-processing treatments. Moreover, this study highlights the challenges associated with the characterization of nanowires structures, where evolution of both surface and bulk composition and structure are extremely important.

5:40pm **AS-WeA11 Compositional Analysis for Additive Manufacturing***, **Michael Brumbach**, N. Argibay, D. Susan, J. Rodelas, J. Reich, B.L. Boyce, A. Roach,* Sandia National Laboratories

The implementation of characterization in additive manufacturing (AM) demands new perspectives for a setting traditionally adapted to support basic science research. As the development of AM continues, the need for diagnostics and control of AM processes is critical and begins with an understanding of materials composition. This exploration of characterization techniques for analyzing bulk composition will give particular consideration for low detection limits, high-throughput analyses, and the ability to quantify light elements. Comparisons between optical emission spectroscopy (OES) from various excitation sources including glow-discharge (GDS), arc-spark, and inductively coupled plasma (ICP) will be discussed. The results are compared to X-ray fluorescence (XRF) and wavelength dispersive spectroscopy (WDS/microprobe). Combustion analysis will be discussed for carbon, sulfur, oxygen, nitrogen, and hydrogen from traditional wrought metals and AM analogs. The role of surface analysis and comparison to bulk techniques will also be demonstrated.

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6:00pm **AS-WeA12 Ambient Mass Spectrometry for the Analysis of Organic Monolayers***, **Han Zuilhof**,* Wageningen University, Netherlands

The characterization of organic monolayers is critically dependent on highly surface-sensitive methods. While a wide variety of methods has been developed over the last decades, *structural information* of organic species, including information relating to their three-dimensional structure, was often very difficult to obtain.

The current presentation sets out to detail the potential of ambient ionization mass spectrometry for this purpose, by giving examples of where it can extend the analysis, where e.g. XPS, scanning probe microscopies and IR fall short.

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