Applied Surface Science
Room 101B - Session AS-MoM

Quantitative Surface Analysis: New Ways to Perform Old Tricks

Moderators: Tony Ohlhausen, Sandia National Laboratory, Carl Ventrice, Jr., SUNY Polytechnic Institute

8:20am **AS-MoM1 Quantitative Analysis of Dendrimer-Encapsulated Nanoparticles***, P. Bhattacharya,* University of Dayton Research Institute*; M.H. Engelhard, L. Kovarik, L. Estevez,* Pacific Northwest National Laboratory*; Y.-C. Wang,* University of Washington*; D.R. Baer,* Pacific Northwest National Laboratory*; D.G. Castner,* University of Washington*;* ***Daniel Gaspar,*** Pacific Northwest National Laboratory **INVITED**

At the nanoscale, quantitatively and accurately measuring material physical and chemical structure remains a fundamental challenge. Many processes essential to energy production or storage, such as catalysis and battery electrochemistry, rely on nanoscale materials with complex three-dimensional structure. In this work, we describe the characterization of ruthenium oxide polyamidoamide (RuO_x-PAMAM) dendrimer-encapsulated nanoparticles (DEN) that have been developed as catalysts for lithium-air batteries. In a lithium-air battery, the RuO_x-PAMAM DENs catalyze the oxygen evolution reaction during charging. The composition and chemical state of the core nanoparticle, and the three-dimensional structure of the DEN are of great interest in understanding and tuning the performance of these materials in Li-air electrochemical cells. X-ray photoelectron spectroscopy (XPS) has become one of the most widely used tools for surface characterization, including quantitative determination of composition. Accurate XPS quantitation requires accurate understanding of electron escape depth, but this information can, in turn, be used for a more detailed understanding of the distribution of elements with depth in a sample. Rudimentary estimates of the electron escape depth in elemental solids have been supplanted by more accurate methods of accounting for chemical differences in electron escape depth. One such tool is the database developed by Powell, et al., called the NIST Database for Simulation of Electron Spectra for Surface Analysis (SESSA), which allows a user to automatically retrieve data needed for a specific practical application and simulate AES and XPS spectra for a multi-layered thin-film or nanoparticle for measurement conditions specified by the user. This database contains extensive sets of data for the physical quantities relevant to AES and XPS. The internal databases are linked to a user interface via a small expert system that allows a user to automatically retrieve data needed for a specific practical application. SESSA can simulate AES and XPS spectra for a multi-layered thin-film sample for measurement conditions specified by the user. In this work, we have used SESSA to help determine the depth distribution of RuO_x and compare to electron microscopy measurements of DEN structure. We have compared the computed model of XPS signal intensity with the experimental measurements.

9:00am **AS-MoM3 Developing a Straightforward Method to Calculate Shell Thicknesses for Core-Shell-Shell Nanoparticles from XPS Data*, David Cant,*** National Physical Laboratory, UK*; Y.C. Wang, D.G. Castner,* University of Washington*; A.G. Shard,* National Physical Laboratory, UK

There is currently great interest in the study of core-shell and core-multi-shell nanoparticles. XPS, as a highly surface sensitive and quantitative analysis method, is potentially of great use in the characterisation of these nanoparticle systems. In particular, understanding the chemical composition and thickness of nanoparticle shells is of great importance for understanding how a given nanoparticle system may interact with its environment. More complicated structures, such as core-shell-shell systems are now commonly studied, whether in the context of core-shell systems affected by adventitious carbon contamination or systems with a core-shell-shell structure by design, and as such there is a need for analysis methods capable of providing quantitative information on the structures of such systems.

Straightforward methods for the characterisation of planar overlayers *via* the use of XPS have been available for some time[1], however such planar analysis techniques are clearly unsuited to providing reasonable estimates of nanoparticle shell thicknesses. Several methods exist for the quantitative analysis of shells in core-shell nanoparticle systems *via* XPS, including by comparison to simulated data[2,3] or by direct calculation from empirical formulae[4]. While comparison to simulation can also be used to characterise core-shell-shell nanoparticles, such methods typically require specialist software or expertise, and are not necessarily easily applicable by the general practitioner of XPS. As such, it is important to consider whether a simpler technique for core-shell-shell systems, accessible to any analyst, can be conceived. While not as straightforward as for the core-shell case, an empirical formula for the calculation of core-shell-shell nanoparticle shell thicknesses has been developed[5] as an extension to the T_{NP} formula[4] for core-shell nanoparticles. This technique requires no specialist knowledge or software, and with a few iterations converges rapidly upon estimates of shell thickness with a deviation typically lower than the error expected in the estimation of the required electron attenuation lengths.

1. Cumpson, P. J. -*Surf. Interface Anal.***29,** 403–406 (2000).

2. Smekal, W., Werner, W. S. M. & Powell, C. J. -*Surf. Interface Anal.***37,** 1059–1067 (2005).

3. Mukherjee, S., Hazarika, A., Santra, P. K., Abdelhady, A. L., Malik, M. A., Gorgoi, M., O'Brien, P., Karis, O. & Sarma, D. D. -*J. Phys. Chem. C***118,** 15534–15540 (2014).

4. Shard, A. G. -*J. Phys. Chem. C***116,** 16806–16813 (2012).

5. Cant, D. J. H., Wang, Y.-C., Castner, D. G. & Shard, A. G. -*Surf. Interface Anal.***48,** 274–282 (2016).

9:20am **AS-MoM4 Double-Lorentzian Asymmetric Line-shape as a Practical Tool for Peak-fitting Multiplet Structures in XPS Data*, Alberto Herrera-Gomez, D. Cabrera-German,*** CINVESTAV-Queretaro, Mexico*; J.A. Huerta-Ruelas,* CICATA-Unidad Queretaro, Mexico*; M. Bravo-Sanchez,* IPICYT, Mexico

The peak-asymmetry commonly found in core level photoemission spectra, especially from transition metals and their oxides, has been described in a number of ways. Doniach and Sunjic (DS) [1] proposed that the asymmetry is due to a "combination of the Kondo effect and a transient and singular re-adjustment of the ground state of the entire Fermi gas to the presence of the effective potential of the hole." The argument was done for metals since the phenomenon requires occupation at the Fermi level. The proposed line-shape, which is extensively employed for peak-fitting, has important shortcomings. The form is not integrable (the area under it is infinite) for any possible value of the associated asymmetry parameter. Since integrability is paramount for composition analysis, the DS line-shape can only be employed in qualitative studies. Another proposed source is the divergence of the energy loss function at zero-loss [2]. Although this argument could apply to both metals and insulators, the divergence in turn causes a divergence in the calculated spectrum, forcing the near-zero loss region to be cut during integration.

A very extended view is that the skewedness is caused by the multiplet structure. Each multiplet component is considered as symmetric and the apparent asymmetry is due to the presence of components of different intensities near each other. In this way it has been possible to qualitatively reproduce the main features (satellites) of a number of materials. An excellent example is the work of Fujii et al. [3] for the Fe 2p spectrum for iron in Fe2O3 and in Fe3O4. As shown in their Fig. 3 and 10, the components are many and distributed with no apparent order. Since the intrinsic width of each component is much larger than the separation among them, it is impossible to experimentally resolve them. In addition, it would not make sense to try to construct a "fundamental" asymmetric line-shape.

Thereupon, we present a practical asymmetric line-shape, the double-Lorentzian (DL) [4], that minimizes the number of parameters employed for fitting complex spectra with apparent peak-asymmetries. The fits are clearly superior than those employing DS and also lacks for the integrability problem. Through DL it is possible to fit theoretical spectra, allowing for the quantitative comparison between the predicted and the experimental data.

1. S. Doniach and M. Sunjic, J. Phys. C 3, 285 (1970).

2. A.C. Simonsen, F. Yubero, S. Tougaard. Phys. Rev. B 56, p. 1612 (1997).

3. T. Fujii, F.M.F. de Groot, G. a Sawatzky, F.C. Voogt, T. Hibma, K. Okada. Phys. Rev. B. 59 (1999) 3195–3202.

4. http://www.qro.cinvestav.mx/~aherrera/reportesInternos/doubleLorentzian.pdf.

9:40am **AS-MoM5 Quantitative Evaluation of the Carbon Hybridization State by Near Edge X-Ray Absorption Fine Structure Spectroscopy**, ***Filippo Mangolini***, University of Leeds, United Kingdom of Great Britain and Northern Ireland; *J.B. McClimon, R.W. Carpick,* University of Pennsylvania

We present a method to determine the carbon hybridization state of carbon-based material using near edge X-ray absorption fine structure (NEXAFS) spectroscopy. Carbon-based materials are of interest due to their exceptional physical and mechanical properties. Characterizing their structure is challenging, but of paramount importance for a wide range of applications.

Of the analytical methods used to characterize the near-surface region of carbon-based materials, carbon 1s NEXAFS spectroscopy is one of the most powerful. However, a critical assessment of the methodology for quantifying the local carbon bonding configuration using NEXAFS data, which is based on the analysis of the sample of interest and of a highly ordered pyrolytic graphite (HOPG) reference sample, is lacking.

In this study [1], the methodology is critically reviewed. Inconsistencies applying this method are found in the literature. A derivation for the correct experimental conditions to be used for acquiring HOPG reference spectra is presented along with the potential sources of uncertainty. Using this, we present a specific method for determining the distribution of carbon hybridization state in a carbon-based material using carbon 1s NEXAFS spectroscopy. As an example, a hydrogenated amorphous carbon film was analyzed. NEXAFS results were compared with results from X-ray photoelectron spectroscopy and Raman spectroscopy. Good agreement was seen, validating our method. This work can assist surface scientists in accurately characterizing the bonding state in carbon-based materials.

1. F. Mangolini, J.B. McClimon, R.W. Carpick, *Anal. Chem.*, 88 (5), 2817, 2016.

10:00am **AS-MoM6 Simultaneous XPS-UPS Depth Profiling of Thin Films**, ***Jon Treacy***, *C. Deeks, P. Mack, T.S. Nunney,* Thermo Fisher Scientific, UK

Thin films have found use in the fields of microelectronics, coatings and photovoltaics, amongst others and continued research is of vital importance in order to improve their performance in these applications. X-ray Photoelectron Spectroscopy (XPS) is a long established technique for analysing these types of samples due to its chemical specificity and surface sensitivity. The closely related technique, Ultraviolet Photoelectron Spectroscopy (UPS), has also been widely utilised to provide detailed valence electronic information with greater surface specificity than XPS, due to the incident radiation being of lower energy.

While useful information is acquired from XPS and UPS in isolation, a more powerful insight into the structure of a material comes from using these two techniques in conjunction, allowing a more complete material characterisation to be performed. Previously, switching between techniques throughout the course of an experiment has been an involved and often laborious process, discouraging more widespread use. Recently the automation of UPS has allowed concurrent acquisition of XPS and UPS data during depth profiling, providing a much sought after insight into the correlation between chemical and electronic structure at within a substrate at various depths.

Of particular interest is the ability to access the valence electronic structure at mixed oxide interfaces using small argon ion gas clusters, which was not previously possible due to the loss of electronic structure in semiconductors or organic materials on exposure to monatomic argon ion beams. This presentation demonstrates the wealth of information that can be acquired by performing XPS-UPS depth profiles and the ease with which this information can be acquired and processed, due to recent instrumentation and software developments.

11:00am **AS-MoM9 Quantification of the Layer Thickness of Thin Organic Layers by Secondary Ion Mass Spectrometry Depth Profiling**, *M.P. Seah,* ***Rasmus Havelund***, *I.S. Gilmore,* National Physical Laboratory, UK

Secondary ion mass spectrometry depth profiling using argon gas cluster sputtering is increasingly applied for the analysis of organic materials including layer stacks used in organic electronic devices. The depth profiles provide valuable information about layer diffusion, segregation, chemical degradation and contaminants in the stack but are generally not quantitative.

We report a study of the quantification of the amount of matter by secondary ion mass spectrometry (SIMS) when depth profiling a nominally 3.1 nm delta layer of fmoc-pentafluoro-L-phenylalanine in Irganox 1010. The depth profiles are made using 5 keV Ar_{2300}^+ sputtering with analysis by 25 keV ions. Data for 89 negative secondary ions shows profiles whose integrated areas, when normalized to the intensity for the pure material, vary over a factor of 12. This variation mainly arises from matrix effects that are measured here using separate samples with mixed layers of 3 intermediate compositions of the two materials. Strong effects can cause the delta layer signal to show structure that may be misinterpreted. The compositional profile is established by using trial profiles, representing the composition, which are then enhanced or reduced according to the measured matrix effect and the result is fitted to the normalized intensity data. It is critical to include the roughening caused by the ion beam. When this is included, the amount of matter is found to be equivalent to 3.25 ± 0.05 nm.

It is concluded that the matrix terms used are a good description of the phenomenon and that SIMS profiles may be made quantitative if suitable secondary ions are available and the matrix terms measured.

11:20am **AS-MoM10 Spectromicroscopy and Vector Analysis of Carbon Materials**, ***Adam Roberts***, Kratos Analytical Limited, UK; *N. Fairley,* Casa Software Ltd, UK; *J.D.P. Counsell, C.J. Blomfield,* Kratos Analytical Limited, UK

Material characterisation by photoelectron spectroscopy is an established technique with a wealth of published data. With the improvement in spectrometer performance spectra are routinely acquired from areas with diameters in the tens of microns, although most routine analysis is performed at much larger areas. Spectra averaged over an analysed area assume a material is homogeneous over this probed area although this might not be true [1,2]. Information from lateral and in-depth distributions [3] for elemental and chemical states on a surface can be probed using XPS imaging either at a single binding (kinetic) energy or over a narrow energy range corresponding to a core-level photoemission peak.

A relatively new and under exploited approach for materials surface characterisation is multispectral XPS imaging, also referred to as spectromicroscopy, where a series of images incremented in energy such that each pixel contains a spectrum. A great advantage of this approach is that spectral information can be reconstructed from defined areas which are smaller than those possible with focused x-ray or virtual probe selected area XPS. Furthermore intensity may be classified by pixel location and binding energy, and summed to reveal multiple spectral forms from a measurement. These spectral forms are ideal for a novel vector method used to identify spectral components characteristic of a material [4,5]. Analysis of the spectra-from-images where the reconstructed spectra are no longer averaged over the total area from which the image is acquired is central to the success of the vector analysis approach. This allows both sample and instrument dependent differences to be 'removed' from the data.

Development of data processing to support spectromicroscopy data reduction has been necessary and a number of approaches have been successfully applied in the characterisation of model and real-world samples[6,7]. This approach has been extended to the interpretation of C 1s spectra for carbon based materials from purely sp^2 graphite and a small number of polymeric materials. As part of this study the influence of sputter cleaning such materials using Ar$^+$ ion gas clusters is also presented.

[1] S. Béchu ***et.al*** Surf. Interface Anal., 2016,48,301-309

[2] E.F. Smith ***et.al*** Surf. Interface Anal. 2005, 38, 69-75

[3] J. Walton, *et.al* Surf. Interface Anal. 2016, 48, 164–172

[4] J. Baltrusaitisa, *et.al*, Applied Surface Science 326 (2015) 151–161

[5] M. d'Halluin, *at.al*, 2015 Carbon, 93, 974 -983

[6] J. Walton, *et.al,* Surf. Interface Anal. 2008, 40, 478 - 481

[7] A.J. Barlow ***et.al***, Surf. Interface Anal. 2015, 47, 173-175

11:40am **AS-MoM11 Angular Broadening in Core Electron Spectroscopy**, *H. Cohen,* Weizmann Institute of Science, Israel; ***Alon Givon***, Tel Aviv University, Israel

Using an analytic approach, the role of angular broadening in quantitative core-electron spectroscopy is investigated. It is shown why, practically, the broadening effect remains relatively small for a broad range of parameters, including detection angular openings of nearly +- 30 degrees. Based on the analytic expression, a correction factor can be derived, suggesting that the replacement of inelastic-mean-free-path by an effective attenuation-length parameter is not necessarily an optimal choice. The derived expression further proposes useful insight on the contribution of leading experimental parameters and, in particular, on the sharp increase of elastic-scattering corrections above a (depth dependent) critical angle.

Author Index

Bold page numbers indicate presenter