Applied Surface Science Division
Room 204 - Session AS+SE-ThM

Applied Surface Analysis of Novel, Complex or Challenging Materials

Moderators: Michael Brumbach, Sandia National Laboratories, Thomas Grehl, ION-TOF GmbH, Germany

8:00am **AS+SE-ThM-1 Understanding the Surface of Complex Oxides used in High Temperature Electrochemical Devices***, **John Kilner**,* Imperial College London, UK*; J Druce,* International Institute for Carbon Neutral Energy Research (I2CNER), Japan*; H Tellez, A Staykov,* International Institute for Carbon Neutral Energy Research (I2CNER) **INVITED**

High temperature electrochemical devices, such as solid oxide fuel cells and electrolyzers, have been under development for application in clean energy systems for many years. Although acceptable performance can be achieved, the requirements of low cost and high durability have been a major hurdle to commercialization. This has necessitated a lowering of the operating temperature from circa 800-900ºC, to temperatures in the region of 500-600ºC, with a consequent loss of electrochemical activity of the electrodes, particularly the air electrode. Key to optimizing performance is gaining an understanding of the gas/solid interface between the Mixed Ionic Electronic Conducting (MIEC) electrodes and the oxygen-rich ambient, and how the structure, composition and activity evolves with time. We have used a multifaceted approach to probe the surfaces of ceramic mixed conductors, after treatment in typical SOFC cathode operating conditions. This has involved ion beam based techniques such as Low Energy Ion Scattering (LEIS) to sample the composition of the outermost atomic layers of ceramic materials, Secondary Ion Mass Spectrometry (SIMS) to measure oxygen exchange activity, complemented by Density Functional Theory (DFT) to clarify possible mechanisms.

The surface termination of substituted (AA')(BB')O_3perovskite-based MIEC materials, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO3\text{-}\delta$ (LSCF), has been studied using LEIS [1] and shown to be dominated by A cations and oxygen, and in particular by segregation of the Sr substituent. For selected (AA')(BB')O_3 compositions, we have investigated the rate of oxygen exchange and shown changes in surface activity that are related to changes in surface chemistry. We have used the knowledge gained from experiment to guide theoretical investigations, to aid in the optimization of candidate air electrode materials. This theoretical study was performed using DFT to simulate the interaction of an oxygen molecule with representative AO and A'O segregated surfaces [2,3].

This combination of theoretical studies guided by advanced surface analysis techniques (i.e. LEIS and SIMS) is enhancing our understanding of processes which determine the performance of these important clean energy devices.

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[2] A. Staykov, H. Téllez, T. Akbay, J. Druce, T. Ishihara, J. Kilner, *Chemistry of Materials***27**(2015) (24) 8273.

[3] T. Akbay, A. Staykov, J. Druce, H. Téllez, T. Ishihara, J.A. Kilner, *Journal of Materials Chemistry A***4**(2016) (34) 13113.

8:40am **AS+SE-ThM-3 Vectorial Method used to Monitor a XPS Evolving System: Titanium Oxide Thin Films under UV Illumination***, S Bechu,* Institut Photovoltaïque d'Ile-de-France, France*; N Fairley,* Casa Software Ltd, UK*; L Brohan,* Institut des materiaux Jean Rouxel, France*; **Vincent Fernandez**,* Université de Nantes, Institut des matériaux Jean Rouxel, France*; M Richard-Plouet,* Institut des matériaux Jean Rouxel, France

1. Introduction

Third generation solar cells aims at increasing efficiency to overtake the 31% theoretical efficiency of simple junction photovoltaic cells established by Shockley and Queisser . According to Marti and Luque [1] , intermediate band cell concept could increase the photocurrent via the absorption of sub-bandgap photons without degrading the voltage. In this perspective, we developed hybrid photosensitive sols-gels based on titanium complexes with specific optical and electronic properties [2] . Once illuminated under UV light, an intermediate band (IB) appears in the band structure so the absorption spreads over visible to near infrared due to reduction of Ti(IV) in Ti(III) [3] and leads to several important changes in the titanium oxide based nanomaterial chemistry. Thanks to this absorption range increase, these gels could be used as active layers in solar cells.

2. Analysis applied to characterize chemical modifications

In order to get insight in the chemical modifications induced by the creation of the IB, XPS experiments were conducted on thin films while UV illumination was performed *in situ*. We present here a new mathematical method which can be applied to XPS measurements when an evolving set of data is recorded: the vectorial method [4,5]. In this case this method is applied simultaneously to Ti 2p and O 1s XPS peaks [6]. From the data set analysis, we established that each of the two Ti(IV) and Ti(III) signals can be split into two components: one Ti(IV) at 458.4 eV is associated to one Ti(III) at 457.1 eV whereas, under UV illumination, a second Ti(IV) peak appears and evolves similarly than a second Ti(III) peak, at 458.1 and 456.7 eV respectively. Those features were obtained from the vectorial method. It was successfully applied to *in situ* UV illumination allowing to get the percentage of thin films photoreduction, the chemical state appearing upon illumination and evolution.

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[2] Cottineau Thomas, Brohan Luc, Pregelj Matej, Cevc Pavel, Richard-Plouet Mireille, and Arčon Denis, Advanced Functional Materials **18**, 2602 (2008).

[3] T. Cottineau, A. Rouet, V. Fernandez, L. Brohan, and M. Richard-Plouet, J. Mater. Chem. A **2**, 11499 (2014).

[4] J. Baltrusaitis, B. Mendoza-Sanchez, V. Fernandez, R. Veenstra, N. Dukstiene, A. Roberts, and N. Fairley, Applied Surface Science **326**, 151 (2015).

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[6] S. Béchu, B. Humbert, V. Fernandez, N. Fairley, and M. Richard-Plouet, Applied Surface Science **447**, 528 (2018).

9:00am **AS+SE-ThM-4 XPS Characterization of Copper and Silver Nanostructures***, **Tatyana Bendikov**, M Susman, F Muench, A Vaskevich, I Rubinstein,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials in terms of elemental composition, chemical and electronic states of the elements and thin layer thicknesses. Here we present examples where XPS analysis provides critical information for understanding the growth and oxidation mechanisms of metal nanostructures.

Studies of solid-state oxidation of copper nanoparticles (NP) by in-situ plasmon spectroscopy complemented by electron microscopies showed formation of oxide/(metal+void) core-shell structure.[1] XPS analysis allows us to unambiguously identify the presence of both CuO and Cu_2O phases in the oxide shell, and to calculate the relative thicknesses of each layer. These data, in combination with electrochemistry, provide proof for a quantitative model of Cu NPs oxidation.

In a recent study, we investigated the mechanism of the electroless formation of nanostructured silver nanoplatelet (NPL) films in the presence of a Fe(III)-tartrate complex.[2] Electron microscopy and XRD showed that NPLs are formed by secondary nucleation on the edges, while nucleation on the flat (111)-oriented faces is suppressed. XPS analysis of NPLs confirmed strong Fe(III)-tartrate adsorption to the Ag NPS surface. XPS studies of the Fe chemical environment reveal the possible formation of polymeric complexes in the adsorbed layer, which may explain the almost complete inhibition of secondary nucleation on the flat (111) surfaces of Ag NPLs.

References:

1. M. D. Susman, Y. Feldman, T. A. Bendikov, A.Vaskevich, I. Rubinstein, *Nanoscale*, **2017**, 9, 12573-12589.

2. F. Muench, A. Vaskevich, R. Popovitz-Biro, T. Bendikov, Y. Feldman, I. Rubinstein, *Electrochim. Acta*, **2018**, 264, 233-243.

[*] Prof. Israel Rubinstein deceased on October 21, 2017.

9:20am **AS+SE-ThM-5 Quantification of Hydroxyl, Major Element and Trace Element Concentrations in Oxide Glasses by Quadrupole SIMS.***, **Albert Fahey**, A Sarafian, T Dimond,* Corning Inc.

Major and trace element calibrations have been established for positive and negative secondary ions measured by Quadrupole SIMS. A Cs+ primary ion beam is used exclusively and element secondary ions are measured directly, not by the MCs+ method. This affords greater sensitivity and is better matched to the operating characteristics of a quadrupole mass spectrometer than by using MCs+ for positive ion species only. Both natural well-studied geologic glasses and Corning research glasses that have been thoroughly characterized have been used to establish the calibrations.

The CAMECA 4550 Quadrupole SIMS is well-suited to measurement of oxide glasses. Charge-compensation is easily achieved for a Cs+ primary beam on uncoated samples of almost any size. This allows the measurement of concentration of species in the surface of glass (from a few nanometers to several micrometers) that can have a significant impact on the physical and chemical durability of the glass. Because oxide glasses contain oxygen as their major element both positive and negative ions can be generated by sputtering with Cs. Although the use of a Cs primary ion beam is generally associated with measurement of negative secondary ions or the use of MCs+ secondary ions, the presence of oxygen in the glass allows production of a significant quantity of positive ions yielding linear calibrations for species that typically would produce positive secondary ions with an oxygen primary beam. Of course, secondary negative ions are produced as well and for the appropriate elements and small molecular ions yield linear calibrations as well.

Detection limits and details of the calibrations will be shown and discussed and examples-measurements of near surface composition changes in various oxide glasses will be shown. Connections of surface chemistry to other glass-properties will be made and explained.

9:40am **AS+SE-ThM-6 Modification of Sputtered Carbon Surfaces in Biosensor Arrays***, **Varun Jain**, M Linford,* Brigham Young University

We describe the chemical modification of carbon surfaces with an eye towards employing them in biosensor (DNA) arrays. Carbon was deposited in thin film form by DC and HIPIMS magnetron sputtering. These depositions were confirmed by atomic force microscopy step height measurements. As indicated by X-ray photoelectron spectroscopy (XPS), the resulting material contained some oxidized carbon at its surface, including –COOH type moieties. These groups could be directly activated for amine attachment using a combination of a carbodiimide (EDC) and sulfo -N-hydroxysuccinimide. Direct attachment of a variety of amines was then possible on this surface, where this process could be followed through the N 1s XPS signal. The surfaces were also activated by direct chlorination using PCl_5, where this process could again be followed by XPS – XPS revealed the introduction and disappearance of chlorine. That is, the chlorine on the resulting carbon surfaces could be nucleophilically replaced with a variety of amines. The DC and HIPIMS sputtered carbon films showed different numbers of reactive functional groups, and the HIPIMS carbon shows unusually smoothness and density by scanning electron microscopy.

11:00am **AS+SE-ThM-10 The Role of Surface Analysis in Characterization of Synthetic Opioids: TOF-SIMS imaging of Fentanyl and Fentanyl Analogs for Forensics and First Responder Safety***, **Greg Gillen**, S Muramoto, J Verkouteren, E Sisco,* National Institute of Standards and Technology (NIST)

The misuse and addiction to opioids including heroin and synthetic opioids such as fentanyl and its various analogs has become a national crisis. Drug overdoses have become the leading cause of death for Americans under the age of 50 with 64,000 overdose related deaths in 2016. The extreme potency of fentanyl and its analogs (100-10,000 times more potent than morphine) may result in even very small doses causing life threatening overdoses. The potency is also a safety concern due to the potential for accidental exposure of law enforcement, first responders, forensic lab personnel and health care providers. To address this concern, several trace chemical analysis techniques are being evaluated as presumptive methods for identification of a suspected opioid while minimizing exposure to end users (1). In addition, since the bulk of illicitly manufactured fentanyl enters the US via overseas mail, there is interest in application of the same chemical screening techniques for detection of fentanyl residues on packages to support interdiction. To facilitate the continued development, evaluation and optimization of the aforementioned screening tools, TOF-SIMS imaging and mass spectral analysis is being used to characterize the particle size and chemical composition of fentanyl and related compounds produced by solution casting of pure materials onto metal substrates or as particles collected on conductive adhesive tapes after sampling the outsides of packages containing suspected opioids. TOF-SIMS was able to image and provide unique mass spectral signatures from individual particles of heroin, fentanyl and several analogs. In order to increase the sensitivity of TOF-SIMS for particle identification, we have evaluated the use of acidic polymer substrates (Nafion) as proton donating particle collection substrates. Preliminary results suggest orders of magnitude improvements in protonated secondary ion signals for fentanyl. Finally, the screening technologies being developed were not designed with consideration of the significant toxicity of fentanyl and fentanyl analogs in the form of respirable aerosols. In a typical screening analysis, thermal desorption from a collection swipe can lead to the formation of aerosols in micrometer size range posing a possible risk of toxic exposure to the analyst. TOF-SIMS was also used to characterize the size distribution of thermally desorbed aerosols emitted by these techniques.

(1). Edward Sisco, Jennifer Verkouteren, Jessica Staymates and Jeffrey Lawrence, *Forensic Chemistry*, (4), 108-115 (2017).

11:20am **AS+SE-ThM-11 3D TOF SIMS, Parallel Imaging MS/MS, and XPS Analysis of Glitterwing (*Chalcopteryx rutilans*) Damselfly Wings***, **Ashley Ellsworth**, D Carr, G Fisher, B Schmidt,* Physical Electronics*; W Valeriano, W Rodrigues,* UFMG, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) damselfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for damselflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C_{60}^+ and large cluster Ar_n^+. With the recent addition of MS/MS capabilities, a conventional TOF-SIMS (MS1) precursor ion analysis and tandem MS (MS2) product ion analysis of targeted precursor ions may be acquired simultaneously and in parallel. The parallel imaging MS/MS is a powerful tool allowing for unambiguous peak identification and provides the maximum information from a given analytical volume.

Here, we explore the use of MS/MS to characterize the chemical composition of the waxy cuticle present on the outer surface of the damselfly wing. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals. [2] Further, we will compare and contrast XPS large cluster Ar_n^+ depth profiling results to reveal the complementary nature of the two techniques.

[1] W.W.Valeriano, Masters dissertation, UFMG, 2016. Retrieved from http://www.fisica.ufmg.br/posgrad/Dissertacoes_Mestrado/decada2010/wescley-valeriano/WescleyWalisonValeriano-diss.pdf.

[2] D. M. Carr, A. A. Ellsworth, G. L. Fisher, et al., Characterization of natural photonic crystals in iridescent wings of damselfly Chalcopteryx rutilans by FIB/SEM, TEM, and TOF-SIMS, Biointerphases 13 (2018), 03B406.

11:40am **AS+SE-ThM-12 Characterization of Aniline Dyes in the Modern Colored Papers and the Prints of José Posada***, J Hedlund, L Gelb, **Amy Walker**,* University of Texas at Dallas

José Posada was a Mexican artist active during the turn of the 20th century, and is often called the father of modern Mexican printmaking. Many of his prints (“broadsides”) have vivid colors but are in urgent need of repair. The dyes that give these broadsides their colors are aniline dyes which are soluble in many solvents. Solvents are often used in paper conservation for the removal of pressure-sensitive tapes, and so treatment protocols that preserve these colors are needed. To develop these methods the aniline dyes need to be identified and characterized.

Dye identification requires either non-destructive *in situ* techniques, such as Raman spectroscopy, or *ex situ* techniques with very high sensitivity; only extremely small samples can be taken in order to preserve the integrity and appearance of the broadsides. Although Raman spectroscopy has been employed to analyze Posada prints it has only limited success especially in the analysis of blue and yellow dyestuffs.

We present a new strategy for analyzing dyed paper samples using secondary ion mass spectrometry (SIMS) and analysis of the resulting data using maximum *a posteriori* (MAP) reconstruction. To test our protocol, we first characterized modern cotton paper colored with a range of aniline dyes. Subsequently we analyzed fiber samples taken from Posada prints. Using SIMS, we are able to identify the dyes used in Posada prints, including hitherto unidentified blue and yellow dyes. Furthermore, MAP analysis provides not only unambiguous identification of the dye adsorbed in the paper by comparison with pure-dye reference samples, but also the characteristic mass spectrum of the paper itself.

12:00pm **AS+SE-ThM-13 GaAs and Si Surface Energies derived from Three Liquid Contact Angle Analysis (3LCAA), as a Function of Oxygen Coverage for Heterogeneous Nano-Bonding^{TM}**, ***Sukesh Ram***, Arizona State University; *K Kavanagh,* Simon Fraser University, Canada; *F Ark, C Cornejo, T Diaz, M Bertram, S Narayan, J Day, M Mangus, R Culbertson, N Herbots,* Arizona State University; *R Islam,* Cactus Materials, Inc.

Native oxides used as surface passivation during semiconductor processing hinder the formation of high quality epitaxial layers. In this research, the surface energies and oxygen content of native oxides of Si(100) and GaAs(100) are measured before and after surface processing prior to a wafer bonding process at T<220°C, "NanoBonding™" [1,2]. Based on Van Oss's theory, Three Liquid Contact Angle Analysis (3LCAA) yields the total surface energy, y^{T}, of semiconductors and insulators. Van Oss models y^{T} as combining of molecular interactions or "Lifshitz-Van der Waals" energy y^{LW} with the energy of interaction with electron donors, y^{+},and acceptors, y^{-}. A new automated image analysis algorithm, "Drop and Reflection Operative Program"(DROP), enables fast, accurate and reproducible extraction of contact angles without subjectivity, reducing to <1° the typical ~5° error between contact angles measurements due to manual extraction. Using for each wafer, a minimum of 12 to 30 drops yields 48 to 120 contact angles, yielding y^{T} , y^{LW}, y^{+} and y^{-} with accuracies better than 3%. By using Ion Beam Analysis (IBA) combining <111> channeling in (100) crystals with the 3.039 ± 0.01 MeV (^{16}O, ^{16}O) nuclear resonance, oxygen coverage can be measured with ML accuracy before and after processin, via SIMNRA simulations, correlating oxygen coverage to data within 1%.

Boron-doped p^{-}Si(100) is found to be always hydrophilic pre-etch, with a y^{T} of 53 ± 1.4 mJ/m^{2}. After an aqueous HF (1:20) etch, y^{T} decreases 10% to 48 ± 2.6 mJ/m^{2}, and Si is hydrophobic. GaAs(100) is initially always very hydrophobic with a y^{T} of 37 ± 2.0 mJ/m^{2}. After etching, Te-doped n+GaAs always becomes hydrophilic with a y^{T} increase of 50% to 66 mJ/m^{2} ± 1.4 mJ/m^{2}. Native oxides on B-doped p^{-}Si(100) wafers are found by IBA to contain 13.3 x 10^{15} at/cm^{2} or 13.3 ± 0.3 oxygen monolayers (ML). After an aqueous HF (1:20) etch, Si(100) exhibits only a 11.6 ± 3% reduction in oxygen to 11.8 ± 0.4 ML . GaAs native oxides contain 7.2 ± 1.4 oxygen ML. After a proprietary passivation-based etch, GaAs native oxides are reduced 49.1 ± 4% to 3.6 ± 0.2 oxygen ML without change in GaAs surface stoichiometry.

3LCAA can quantify accurately the reactivity of a surface before Nano-Bonding^{TM}, which can be correlated to oxygen coverage and structure. High-resolution IBA and 3LCAA allows for a quantitative analysis of Si and GaAs surfaces energies as function of surface processing, enabling for the engineer interactions between surfaces for NanoBonding.

1. Herbots N. *et al*. US Pat. N^{o} 9,018,077 (2015), US Pat. N^{o} 9,018,077 (2017)

2. Herbots N., Islam R., US Pat. Pending (2018), filed March 18, 2018

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