

Applied Surface Science Division Room A211 - Session AS+BI+RA-MoM

Quantitative Surface Analysis I/Reproducibility Issues in Quantitative XPS

Moderators: Donald Baer, Pacific Northwest National Laboratory, Mark Engelhard, Pacific Northwest National Laboratory

8:20am **AS+BI+RA-MoM1 Improving Accuracy in Quantitation by XPS: Standards, Cross-sections, Satellite Structure, C. Richard Brundle, C.R.Brundle & Associates; P.S. Bagus, University of North Texas; B.V. Crist, XPS International LLC** **INVITED**

Determining elemental composition by XPS requires determining relative peak intensities from the elements concerned, and then normalizing using Relative Sensitivity Factors (RSF's). Such RSF's are usually generated from standard materials using the intensity from the "main" peak only and ignoring any associated satellite structure (shake-up, shake-off, and multiplet splitting components) intensity. In the seminal paper by Wagner, et al, (1) this resulted in a conclusion that the calculated Li(1s) photoionization cross-section, σ , (2) was too low by ~40%, relative to F(1s). This apparent discrepancy cast doubt on the claimed 5% accuracy of the calculated σ values for low Z elements (2). We show that this is incorrect. The discrepancy is due, primarily, to the fact that Li(1s) loses almost zero intensity from the main peak into associated satellites, whereas for F1s it is substantial, *spreading over 100eV to lower KE*. A calculated σ always refers to the *total* intensity of photoemission from the orbital concerned, including any intrinsic satellite structure. In addition, the experimental Li(1s) peak intensity in Wagner, et al. (1) was actually *overestimated*, owing to inclusion of overlapping satellite structure spreading from the nearby F(2s) peak. For the 1s intensities of the first row elements, a crude theoretical approximation predicts the total intensity lost from the "main" peak to satellites quite well. It involves an exponential dependence on the number of valence shell electrons present, which for Li+ of LiF, is zero, and for F- is 6 (the filled 2p shell), yielding values of zero loss for Li+ and 20-30% for F-. Full *ab initio* quantum calculations for these ions support the crude estimate (calculated Li+ losses are 1.4%; F- losses are 22.7%). In contrast to earlier claims to the contrary(3), satellite losses, for elements across the periodic table, vary widely from core-level to core level, element to element, *and most critically with the bonding situation of an element (see, for example ref 4)*. Thus any "universal" element RSF's, using main peak intensities only, though semi-quantitatively useful, are inherently limited in potential accuracy achievable, sometimes by up to a factor of 2. What is needed, for improved accuracy, are sets of RSF's appropriate to different bonding situations. Such sets would be particularly useful for the current large inexperienced XPS user base. We attempt to give guidelines.

C.D. Wagner, et al, Surf. Interface Anal. **3**, 211, 1981

J.H. Scofield, J. Elec. Spec. **8**, 129, 1976

V.G. Yarzhemsky, et al, J. Elec. Spec. **123**, 1, 2001

P. S. Bagus, E. Ilton, and C. J. Nelin, Catalysis Letters, **148**, 1785, 2018

9:00am **AS+BI+RA-MoM3 A Rigorous Approach to the Calculation of the Uncertainties in XPS Analysis, A. Herrera-Gomez, CINVESTAV-Unidad Queretaro, México; Orlando Cortazar-Martinez, CINVESTAV-Unidad Queretaro, Mexico**

One of the most important applications of X-ray photoelectron spectroscopy (XPS) is the characterization of the chemical composition of solids near the surface. However, the proper assessment of the associated uncertainties has remained an elusive problem. One of the issues is that the total uncertainty comes from various sources: the experimental data (peak intensities), parameters theoretically calculated (cross-section, mean-free-path), and parameters associated to the XPS equipment (angular and kinetic energy transmission functions).

The uncertainty on most of these parameters should be treated as systematic errors. The most important non-systematic uncertainty comes from the peak intensities [1]. It is a common practice in XPS data peak fitting to first subtract the background and then peak-fit the backgroundless data (*static* approach [2]). This approach prevents the use of the covariance matrix to calculate uncertainties because the covariance with the parameters defining the background cannot be accounted. It is only under the *active* approach [2] that it is possible to account for the covariance with the background parameters because the background is optimized in conjunction with the peak parameters. In this paper, the

assessment of the uncertainty on the peak intensities will be treated in detail, as well as the total uncertainty on the composition.

[1] A. Herrera-Gomez, A rigorous approach to the calculation of the uncertainties in XPS analysis (Internal Report), Internal Report, Internal Report. CINVESTAV-Unidad Queretaro, n.d. <http://www.gro.cinvestav.mx/~aherrera/reportesInternos/uncertaintiesXP S.pdf>.

[2] A. Herrera-Gomez, M. Bravo-Sanchez, O. Ceballos-Sanchez, M.O.O. Vazquez-Lepe, Practical methods for background subtraction in photoemission spectra, Surf. Interface Anal. **46** (2014) 897–905. doi:10.1002/sia.5453.

9:20am **AS+BI+RA-MoM4 Gross Errors in XPS Peak Fitting, Matthew Linford, V. Jain, G.H. Major, Brigham Young University**

X-ray photoelectron spectroscopy (XPS) is the most important method for chemically analyzing surfaces. It is widely used in numerous areas of research and technology. Many research groups and individuals are skilled at analyzing XPS data. However, too much of what has appeared and continues to appear in the literature is of at best questionable value and accuracy. In this talk, I will discuss some of the all too common gross errors. Both correct and incorrect examples of each of the following will be shown. (i) Not plotting the data according to international convention of binding energy increasing to the left. (ii) Fitting and interpreting data that are far too noisy to be interpreted. (iii) Labeling noise as chemical components. (iv) Not showing the original data – only showing the synthetic (fit) peaks and their sum. (v) Not plotting the sum of the fit components with the original data. (vi) Having widely varying peak widths in a fit. (vii) Having the baseline completely miss the noise on either side of the peak. (viii) Not collecting data over a wide enough energy window to see a reasonable amount of baseline on both sides of the peak envelope. (ix) In a C 1s spectrum, reversing the labeling on the C-O and C=O peaks, and other mislabeling issues. The C 1s peak envelope is well understood so there shouldn't be huge mistakes here. (x) Not taking into account spin-orbit splitting when it is necessary. (xi) In a comparison of spectra, having widely differing peaks and peak positions for components that are supposed to be the same between the spectra.

9:40am **AS+BI+RA-MoM5 Improved Energy Referencing in XPS, Hagai Cohen, Weizmann Institute of Science, Israel**

Basically, energy referencing in XPS relies on an absolute reference provided at the back contact of the sample: the electrical ground. If poor connectivity is encountered between the studied surface and ground, reference signals may be used to derive correction terms for the energy scale, such as to get the proper binding energies for elements of interest. Unfortunately, in many cases this procedure fails to accurately address differential charging effects, namely local and temporal variations in the surface charge and the related electrostatic potential.

In the present work, a method for introducing a second absolute/external reference is described. The technical improvement is proven to be mandatory. It enables advanced analyses of binding energies, which refines the chemical analysis significantly. The method further reveals intriguing cases in which the x-ray induced charging does not follow the trivially expected behavior. On top of that, an access to rich electrical information is realized as soon as a second reference is introduced, thus expanding the XPS capabilities into new areas. Measurements of the inherent inner fields in semiconductors and the reliable derivation of device band diagrams, free of the beam-induced artifacts, are just a few examples to be mentioned.

10:00am **AS+BI+RA-MoM6 How to Avoid Errors in the Interpretation of XPS Data?, Andreas Thissen, P. Dietrich, SPECS Surface Nano Analysis GmbH, Germany; W.E.S. Unger, Bundesanstalt für Materialforschung und -prüfung - Berlin (Germany), Germany**

Over the last fifty years significant developments have been done in photoelectron spectroscopy instrumentation and thus opened new fields of application. Especially XPS or ESCA developed into a standard analytical method in many labs for surface and material characterization. The number of users and the number of publications using XPS data has tremendously increased. But as a side effect it is a challenge to keep the level of knowledge about the method and correct data interpretation at a high level for all users of these data.

To avoid errors in the interpretation of XPS data instrument manufacturers put efforts inside their instruments and software packages to help and guide the user through data acquisition, data quantification and interpretation and finally also through data reporting. By this data can be made compatible with existing ISO and other community standards. But

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even more, data quality becomes transparent also in times of open source publications and open data repositories.

This paper summarizes the challenges of data handling, data treatment, data storage, parameter-data correlation, expert systems for data acquisition, reporting assistance and tracking and authorization tools for sensitive data. In summary future perspectives and suggestions are discussed for improved data repeatability and data reliability.

10:40am **AS+BI+RA-MoM8 Misinterpretations in the Spectroscopic Analysis of Heterogeneous Materials and Defected Structures**, *Lisa Swartz, K. Artyushkova, J.E. Mann, B.W. Schmidt, J.G. Newman*, Physical Electronics

Analysis of samples where lateral heterogeneities can be present at a variety of scales poses a challenging spectroscopic task. In routine applications of XPS spectroscopy, the analyst is usually acquiring spectra over a large area from multiple positions on the sample and derives conclusions on “representative” chemical composition from average atomic concentrations and standard deviations. However, if lateral heterogeneities existing at the surface have smaller physical dimensions as the analysis area, the conclusions on “representative” chemical composition derived from large area spectroscopy will be erroneous. For accurate structural analysis of heterogeneous materials, it is very important to understand the scale of heterogeneity beforehand, so that the analysis areas and the size of the X-ray probe used for analysis are chosen appropriately. Often, complimentary microscopic techniques, such as SEM, are performed before XPS analysis which addresses some of this challenge but does not allow analysis over the same area.

The ability to perform small area spectroscopy for studying the heterogeneity and physical dimensions of samples is critical for obtaining accurate information on sample structure. In this talk, we will show examples of inaccurate use of large area spectroscopy and discuss the experimental approach towards selecting the relationship between the X-ray size and physical scale of defects and heterogeneities at the surface required to obtain an accurate representation of heterogeneous sample structure.

11:00am **AS+BI+RA-MoM9 Current Issues and Solutions for Reliable, Robust and Reproducible XPS Spectral Acquisition and Data Reporting**, *J.D.P. Counsell, C.J. Blomfield*, Kratos Analytical Limited, UK; *Christopher Maffitt*, Kratos Analytical Limited; *N. Gerrard, S.J. Coultas*, Kratos Analytical Limited, UK

XPS is now a truly interdisciplinary technique used in a wide variety of fields including catalysis, tribology, bioremediation and nuclear energy. With more than 1000 instruments currently in use, the ubiquitous nature of XPS means there is a greater requirement than ever for clarity regarding spectral acquisition, analysis and interpretation. The XPS user base has changed significantly – no longer the field of dedicated “technical experts” and spectroscopists – requiring instruments to be simple to use with a higher degree of automation in all parts of operation and analysis.

Here we will discuss the overall procedure for the technique specifying the critical steps in generating sound data and conclusions. Pitfalls and perils in the following steps will be briefly discussed: surface charging, beam damage, contamination, peak identification, energy calibration, quantification, peak-fitting, database usage, chemical state assignment and error reporting as will the latest methods implemented in mitigating against these issues. Worked examples and user studies will be presented to illustrate common inconsistencies.

11:20am **AS+BI+RA-MoM10 Intensity Calibration and Sensitivity Factors for XPS Instruments with Monochromatic Ag L α and Al K α Sources**, *A.G. Shard*, National Physical Laboratory, UK; *J.D.P. Counsell, Christopher Blomfield*, Kratos Analytical Limited, UK; *D.J.H. Cant*, National Physical Laboratory, UK; *E.F. Smith*, University of Nottingham, UK; *P. Navabpour*, Teer Coatings Ltd, UK

The use of monochromated Ag L α X-ray has been described previously.^{1,2} These sources have now become more widely available on commercial instruments and easier to use due to automation and the superior collection efficiency of modern analysers. To enable direct comparison between data acquired using both sources it is essential to be able have a common calibration scheme and a set of useful sensitivity factors. We employ the calibration method developed by the National Physical Laboratory for Al K α sources³ and extend this for Ag L α sources.⁴ Sensitivity factors for Ag L α and Al K α are calculated from photoionisation cross sections and electron effective attenuation lengths. These compare well to previous experimental values and data acquired from ionic liquids. The

intensity of the Ag L α source is found to be approximately 50 times lower than the Al K α source. This, coupled with generally lower photoemission efficiencies, results in noisier data or extended acquisition times. However, there are clear advantages to using the Ag L α source to analyse certain elements where additional core levels can be accessed and for many technologically important elements where interference from Auger electron peaks can be eliminated. The combination of calibrated data from both sources provides direct and easily interpreted insight into the depth distribution of chemical species. This could be particularly important for topographic samples, where angle resolved experiments are not always helpful. We also demonstrate, using thin coatings of chromium and carbon, that the inelastic background in Ag L α wide-scan spectra has a significantly increased information depth compared to Al K α .

References

1. Yates, K.; West, R. *Surf. Interface Anal.* **1983**,5 (4), 133-138.
2. Edgell, M.; Paynter, R.; Castle. *J. Electron Spectr. Rel. Phenom.* **1985**,37 (2), 241-256
3. Seah, M. P.. *J. Electron Spectr. Rel. Phenom.* **1995**,71 (3), 191-204.
4. Shard, A. G. *et al. Surf. Interface Anal.* **2019**<https://doi.org/10.1002/sia.6647>

11:40am **AS+BI+RA-MoM11 Reporting XPS Measurements and How Can We Do Better to Minimize Reproducibility Problems**, *Karen Gaskell*, University of Maryland, College Park

The level of detail and information provided in the average scientific article reporting XPS measurement and analysis varies widely. In some cases journal page limitations limit the inclusion of information such as experimental details, instrumental parameters and data sets that are required to fully describe the data collection and subsequent analysis so that it can be adequately reproduced by others. In other cases important information is simply left out. What are the minimum and preferable types of information we should include when reporting XPS results?

Biomaterial Interfaces Division

Room A120-121 - Session BI+AS+NS-MoM

Biofabrication, Bioanalytics, Biosensors, Diagnostics, Biolubrication and Wear

Moderators: Joe Baio, Oregon State University, Caitlin Howell, University of Maine

8:20am **BI+AS+NS-MoM1 Bio-inspired Peptide-polymer Hybrid Mucin Analogues: Applications in Osteoarthritis and Kidney Stone Disease**, *Daniel L. French, L.A. Navarro, S. Zauscher*, Duke University

Mucins play diverse and crucial roles in the body. These functions range from lubrication of articular joints and the eye, to protection of stomach endothelium, to modulation of oral and gut microflora populations. Despite their diversity, these functions commonly stem from modifications in a general structure shared by all mucins: a blocky polypeptide backbone comprised of terminal moieties for binding surfaces or crosslinking and a characteristic glycosylated bottlebrush. Inspired by this adaptable structure, we have created a mucin analogue platform which engenders key structural features preserved among native mucins. We have emulated the mucinous bottlebrush with a lysine-rich elastin-like polypeptide backbone, which provides primary amines for conjugation of synthetic polymer “bristles.” Binding modules target surfaces of interest, to facilitate intramolecular associations, or to direct surface conformation of our construct. To demonstrate the application of our platform to clinically-relevant problems, we have tailored our mucin analogues to osteoarthritis and kidney stone disease, conditions infamous for profound morbidity and high prevalence. We will demonstrate that collagen-targeted mucin analogues adsorb to model surfaces and prevent protein fouling. This recapitulates the function of lubricin, a mucin downregulated in osteoarthritis. Similarly, we will show that we can target mineral surfaces relevant in kidney stone disease by exchanging the binding module of our analogue mucins. We will show that these altered analogues also inhibit protein-fouling, which is implicated in stone growth. In this platform technology, we have been inspired by the diverse functions of native mucins. By harnessing the general structure which gives rise to these properties, we endeavor not only to replicate the in vivo function of mucins, but also to harness the properties of natural mucins and apply them to systems not naturally protected by mucinous coatings, such as inhibiting the growth of kidney stones.

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8:40am **BI+AS+NS-MoM2 Investigation of the Mechanical and Dielectric Properties of Bone Scaffolds**, *Kimberly Cook-Chennault*, Rutgers University

Despite the vast number of biomaterials and synthesis technologies available to treat bone defects and disease, few are readily employed for clinical use due in part to challenges in the development of materials that functionally mimic and facilitate the hierarchical processes of bone healing and regeneration. Calcium phosphate based bone replacement materials have been developed over the years for bioengineered bone structures due to their ability to mimic the general properties of mineralized bone. These bone replacement materials have mainly be fabricated in the form of hydroxyapatite (Hap), which can suffer from premature fracture when subjected to typical human load conditions. On the other hand, it is well known that enhanced osteobonding and bone growth results from the exposure of the bone to polarized Hap, which presents a negatively charged surface. Composite hydroxyapatite (Hap) – barium titanate scaffold materials are compared and contrasted with hydroxyapatite (Hap) samples for mechanical elastic moduli, compression strength and dielectric properties. Composite structures were observed to present better mechanical and dielectric properties when compared to HAp samples. For example, the elastic modulus of the HAp and composite samples were 2655.4 MPa and 3559.1 MPa, respectively. Understanding the interrelationship between scaffold architecture/material composition and mechano-transduction will improve our ability to realize patient specific solutions that eliminate hindrances to bone healing such as, lack of vascularization and lack of adequate mechanical stability.

9:00am **BI+AS+NS-MoM3 Bioelectronics with Graphene and Graphene-Based Hybrid-Nanomaterials – From Transparent to Fuzzy Interfaces**, *Tzahi Cohen-Karni*, Carnegie Mellon University **INVITED**

We focus on developing a new class of nanoscale materials and novel strategies for the investigation of biological entities at multiple length scales, from the molecular level to complex cellular networks. Our highly flexible bottom-up nanomaterials synthesis capabilities allow us to form unique hybrid-nanomaterials. Recently, we have demonstrated highly-controlled synthesis of 3D out-of-plane single- to few-layer fuzzy graphene (3DFG) on a Si nanowire (SiNW) mesh template. By varying graphene growth conditions, we control the size, density, and electrical properties of the NW templated 3DFG (NT-3DFG). This flexible synthesis inspires formation of complex hybrid-nanomaterials with tailored optical and electrical properties to be used in future applications such as biosensing, and bioelectronics. Currently, we target the limits of cell-device interfaces using out-of-plane grown 3DFG, aiming at electrical recordings with subcellular resolution (<5 μ m). Moreover, NT-3DFG unique optical properties allows formation of remote interfaces with tissue and cells. We demonstrate photostimulation of tissue and cells by using the photothermal effect of NT-3DFG. Last, we have developed a unique transparent graphene-based electrical platform that enables concurrent electrical and optical investigation of ES-derived cardiomyocytes' intracellular processes and intercellular communication. In summary, the exceptional synthetic control and flexible assembly of nanomaterials provide powerful tools for fundamental studies and applications in life science, and open up the potential to seamlessly merge either nanomaterials-based platforms or unique nanosensor geometries and topologies with cells, fusing nonliving and living systems together.

9:40am **BI+AS+NS-MoM5 Experimental Observation of Multiple Plasmon Induced Transparency and Fano Resonance in Titanium Nitride Based Devices**, *J.D. Asencios, Arturo Talledo, R.A. Moro, C.A. Luyo*, Facultad De Ciencias Universidad Nacional De Ingeniería, Perú

Abstract: We built three types of plasmonic structures based on titanium nitride thin films by using the technique dc magnetron sputtering and D-shaped prisms as substrates. The prisms were made of glass or sapphire. Devices with structure Prism/TiN, Prism/TiN/SiO₂ and Prism/TiN/SiO₂/Nb₂O₅ were called devices type 1, type 2 and type 3, respectively. Attenuated Total Reflection in the Kretschmann configuration was studied in the three types of devices. Experimental angular spectra were fitted by using a calculation program based on the solutions to Maxwell equations. ATR spectra of devices type 1 show a wide absorption band. The main feature for ATR spectra of devices type 2 was a series of maxima and minima of reflectance within a wide absorption band. ATR spectra of devices type 3 are identified with a very sharp window within the absorption band. The spectra of devices type 2 and type 3 were associated with the phenomena of Multiple Plasmon Induced Transparency (MPIT) and Fano Resonance, respectively. Based on calculations of the square of the electric fields in the involved media, we proposed some simple phenomenological explanations for the phenomena of MPIT and

Fano resonance. Potential use of these structures as refractive-index sensors was also discussed.

10:00am **BI+AS+NS-MoM6 Breaking the Mass Resolution Limit of Shear Wave Resonators in Liquid through Integrated Microfluidic Channels**, *Z. Parlak, S. Zhao, D.L. French, Stefan Zauscher*, Duke University

Acoustic shear wave resonator sensors (SWRS), e.g., quartz crystal microbalance, are widely used in applications (e.g., thin film deposition) where their high quality factor in air or vacuum provides exquisite mass resolution. SWRS are also used as biosensors in liquid environments; however, they have not yet found widespread use outside the research environment despite their simple and robust detection modality. This is because current SWRS suffer from viscous contributions to shifts in resonance frequency, which inherently leads to low mass resolution. Furthermore, current SWRS require accurate temperature control and use large liquid volumes (~ml). Together these limitations prohibit accurate and economic measurement of surface bound mass, e.g., in protein binding assays. We show through experiments and simulations that by confining fluid into small, rigid channels oriented perpendicularly to the shear direction of the SWRS, we can manipulate liquid to behave as a lossless layer and thus perform precise mass measurements of the confined liquid. Canceling viscous effects in μ -fluidic SWRS not only enhances their mass resolution in liquid to levels observed in air/vacuum, but also enables efficient device miniaturization. Combined with the extremely small volume requirements for sensing (~nL), we show that μ -fluidic SWRS can overcome current barriers for their widespread use in diagnostic sensing and point of care applications.

11:20am **BI+AS+NS-MoM10 All Inkjet Printed Biosensor for Easy and Rapid Detection of Immunoglobulin G (IgG) Protein**, *Ridwan Fayaz Hussain, A.B. Kaul*, University of North Texas

Protein detection biosensors are interesting tools for detecting and measuring the levels of specific proteins in biological and environmental samples, offering certain operational advantages over standard photometric methods, notably with respect to rapidity, ease-of-use, cost, simplicity, portability, and ease of mass manufacture. Although inkjet printed electrode based sensor is widely reported, the number of fully inkjet printed biosensors is still limited [1,2]. Here, we report the design, fabrication, and evaluation of a flexible field-effect transistor (FET) for biosensing based on the inkjet printing technique, where the insulator layer is uniquely functionalized for Immunoglobulin G (IgG) protein detection. IgG is a plasma-cell protein that is produced within the lymph nodes, spleen, bone marrow, respiratory tract mucosa, tissue, etc. Since IgG protein is produced as part of the body's response to bacteria, viruses, and tissue antigens, measurement of blood IgG levels can reveal any of the body's abnormal conditions. Until now, proteins are detected mostly by antibodies in analytical formats like ELISA, immunobead assay, western blotting, and microarrays, etc. but their performance is limited by low sensitivity. This new generation biosensor is more stable and well adapted to the conditions of real samples. The protein detection biosensor reported here represents an important starting point for the design and fabrication of flexible, rapid detection biosensing devices by inkjet printing. This work shows a promising aspect of protein detection that will pave the way for the development of a fully functional device for point-of-care diagnosis.

Reference:

- [1] Jensen, G. C., Krause, C. E., Sotzing, G. A., & Rusling, J. F. (2011). Inkjet-printed gold nanoparticle electrochemical arrays on plastic. Application to immunodetection of a cancer biomarker protein. *Physical Chemistry Chemical Physics*, 13(11), 4888-4894.
- [2] Carvajal, S., Fera, S. N., Jones, A. L., Baldo, T. A., Mosa, I. M., Rusling, J. F., & Krause, C. E. (2018). Disposable inkjet-printed electrochemical platform for detection of clinically relevant HER-2 breast cancer biomarker. *Biosensors and Bioelectronics*, 104, 158-162.

11:40am **BI+AS+NS-MoM11 Biosensing Applications of Silver Nanorods Array Fabricated by Glancing Angle Deposition (GLAD)**, *Shashank Gahlaut*, Indian Institute of Technology Delhi, India

Silver being most widely used material due to its unique electrical and optical properties. Here we have investigated biosensing properties of silver nanorods array (AgNRs) fabricated by glancing angle deposition. GLAD grown silver nanorods are found to be highly sensitive and selective for hydrogen sulfide (H₂S) gas. Color and water wetting (contact angle) of AgNRs array are parameters affected in the presence of this gas. H₂S is one the major gaseous products evolved in bacterial metabolic process. On the

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basic of H₂S production, we have shown the detection of viability as well as antibiotic resistance in different strains of bacteria.

Another potential application of as synthesized AgNRs array in Surface enhanced Raman scattering (SERS) based detection. The dengue is a viral disease and a serious global health concern. About 2.5 billion of world's population has been living at the risk of dengue infection. It causes a spectrum of illness ranges from acute febrile illness called dengue fever (DF) to more severe life threatening forms dengue hemorrhagic fever (DHF) and dengue shock syndrome (DSS) causing vascular leakage that may lead to death. So far, neither specific treatment nor effective vaccine available for the prevention and treatment. Therefore, early detection is the key of the survival of the patients. The earlier symptom starts with mild dengue fever, at this stage the concentration of the biomarkers are very less which pose a problem in early detection. In the present study, we have demonstrated the detection of dengue from clinical blood samples employing AgNRs array as SERS substrates with hand held Raman spectrometer. A notable change in SERS spectral signature observed in the blood of dengue infected patients in comparison to that of healthy subject. This change was further confirmed using the statistical tool principal component analysis (PCA) and the samples were differentiated as healthy, dengue positive and dengue negative. All the blood samples were also dually verified with Antigen (NS1) as well as Antibody (IgM) ELISA kit. This method provides a field deployable, rapid diagnosis of dengue at its early stage.

Biomaterial Interfaces Division

Room A120-121 - Session BI+AS-MoA

Cutting Edge Bio: Bio-Nano, Bio-Energy, 3D Bio

Moderators: Heather Canavan, University of New Mexico, Jordan Lerach, ImaBiotech Corp.

2:20pm BI+AS-MoA3 Antimicrobial Cyclic Peptide Polymer Nanopores, *Kenan Fears, L. Estrella*, US Naval Research Laboratory

We present a new class of bioinspired nanomaterials that are stabilized by a combination of covalent and hydrogen bonds. Prior work by others has shown that cyclic peptides can self-assemble to form supramolecular assemblies through backbone-backbone hydrogen bonding. To improve upon this molecular architecture, we develop a synthesis route to polymerize cyclic peptides and form a linear polymer chain that can transition between a rigid nanorod and a "soft" unfolded conformation. For a cyclic peptide polymer containing amine-terminated side chains on each ring, we demonstrate self-assembly can be triggered in aqueous solutions by varying the pH. We measure the elastic modulus of the rigid nanorods to be ca. 50 GPa, which is comparable to our molecular dynamics (MD) prediction (ca. 64 GPa). Our results highlight the uniqueness of our molecular architecture, namely their exemplary toughness (up to 3 GJ m⁻³), in comparison to other cyclic peptide-based assemblies. Finally, we demonstrate the amphiphilic cyclic peptide nanopores are capable of inserting into the membrane of both gram-negative and gram-positive bacteria, and causing their deaths by disrupting their osmotic pressure.

2:40pm BI+AS-MoA4 ToF-SIMS Analysis of the Distribution of *p*-Hydroxybenzoate in Wood, *Robyn E. Goacher*, Niagara University; *Y. Mottiar*, University of British Columbia, Canada

The progress towards a green bio-based economy depends in part on our ability to chemically modify lignocellulosic plant matter. Possible targets for such chemical modifications include ester-linked pendant groups that occur on lignin in some plant species. The lignin in poplar and willow is known to contain 1-10% of *p*-hydroxybenzoate (*p*-HB) moieties, although little is known about the function of these *p*-HB groups. To understand the function of *p*-HB, it is important to understand the distribution of *p*-HB among different cell types. Previous work with ultraviolet microscopy suggests that *p*-HB is present only in fibers and not in vessels. The goal of this work is to provide a more specific analysis of the spatial distribution of *p*-HB in wood by using surface-sensitive chemical imaging. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) was used to image cross-sections of mature Lombardy poplar, juvenile (greenhouse-grown) Lombardy poplar and mature DUKE-5 willow. Lombardy poplar is known to contain higher levels of *p*-HB than the DUKE-5 willow. Samples were analyzed prior to and after solvent extraction to remove spectral interferences from small molecule extractives, which have similar chemical composition to *p*-HB and lignin. A milk alkaline hydrolysis was also performed to cleave ester-linked *p*-HB from lignin in order to confirm identification of certain peaks within the mass spectra as characteristic of *p*-HB. Multivariate statistical analysis was used to aid in the data interpretation. The process of identifying peaks that arise from *p*-HB will be discussed, and chemical images of the localization of *p*-HB will be presented. This data contributes to our understanding of how *p*-HB is distributed in wood. These insights may shed light on the role of ester-linked moieties in lignin and will hopefully advance the use of *p*-HB as a biotech target.

3:00pm BI+AS-MoA5 Feeling the Force; Probing the Cues that Influence Stem Cell Behaviour, *Stephanie Allen*, School of Pharmacy, The University of Nottingham, UK

INVITED

There is considerable research activity directed towards understanding the basic biology of stem cells and controlling their mechanisms of self-renewal and differentiation into functional tissue types. Much of the current research involves genetic and/or biochemical approaches to control proliferation and differentiation. Over the last decade, studies using biophysical approaches, including our own, have begun to impact on this understanding, revealing that physical signals and cues elaborated by neighbouring cells and the surrounding extra-cellular matrix, are also fundamental to controlling stem cell fate (1-4). For many emerging approaches/applications, including those that aim to create functioning tissues through the 3D patterning of stem cells, an understanding of such physical cues is therefore vital.

Despite this importance relatively few studies have still attempted to investigate and quantify the physical interactions between stem cells and/or the effects of applied stimuli. This talk aims to provide an overview of our recent research in this area, that aims to address this knowledge gap by utilizing force measurement approaches (including optical tweezers and atomic force microscopy). The presentation will include results from a current project where we are employing AFM-based single molecule force measurement approaches to provide new insights into the role of cadherins on mouse embryonic stem cells (mESCs).

- (1) Discher *et al Science* 324 :1673-1677 (2009)
- (2) Lanniel *et alSoft Matter*. 7, 6501-6514 (2011)
- (3) Lanniel *et alThin Solid Films* 519, 2003-2010 (2011)
- (4) Kirkham *et alScientific Reports*, 5, No. 8577 (2015)

4:20pm BI+AS-MoA9 Angstrom-Resolved Characterization of Electrochemical Interfaces in Real Time during Polarization, *Markus Valtiner*, Vienna University of Technology, Austria

Electrochemical solid|liquid interfaces are critically important for energy conversion, biosensing and biodegradation processes. Yet, a real-time visualization of dynamic charging processes at electrified solid|liquid interfaces with close to atomic resolution is extremely challenging.

I will discuss a unique real-time atomistic view into dynamic charging processes at electrochemically active metal interfaces using white light interferometry in an electrochemical surface forces apparatus. This method allows simultaneous deciphering of both sides of an electrochemical interface; the solution and the metal side; with microsecond resolution under dynamically evolving reactive conditions that are inherent to technological systems in operando. The real-time capability of this approach reveals significant time lags between electron transfer, oxide reduction/oxidation, and solution side reaction during a progressing electrode process. In addition, the developed approach provides detailed insight into the structure of the electric double layer under varying charging conditions. I will also discuss how we can complementary use high resolution in-situ AFM imaging to further characterize ion layering at charged surfaces.

The presented work may have important implications for designing emerging materials utilizing electrified interfaces and may apply to bio-electrochemical processes, signal transmission and pore charging.

Applied Surface Science Division

Room A211 - Session AS+BI+RA-TuM

Quantitative Surface Analysis III/Other Surface Analysis Methods

Moderator: Karen Gaskell, University of Maryland, College Park

8:00am **AS+BI+RA-TuM1 Oxygen Energy Filtering and Relative Sensitivity Factor Considerations for Making U and Pu Measurements by LG-SIMS, Todd Williamson**, Los Alamos National Laboratory **INVITED**

During nuclear facility inspections, inspectors collect materials intended to show a history of the operations that have taken place within a facility.

These materials can be particles obtained using cotton swipes, solid discarded or operationally related nuclear materials, or other items contaminated with nuclear materials. Analysis of these samples is an extremely powerful tool with which to determine facility operations and history. Uranium analysis by SIMS is a mature technique used by the IAEA and its Network of Analytical Laboratories for treaty verification. The analysis of mixed uranium-plutonium particles and solids is not as mature as a capability and has been identified by the IAEA as topic for increased R&D.

This presentation will cover two technical topics related to the analysis of mixed uranium-plutonium materials, relative sensitivity factors (RSF) and energy filtering to improve hydride correction. For a material that contains both U and Pu, while both elements will be sputtered and become ionized during SIMS analysis, they will do so with different efficiencies. This ionization difference tends to be sample-type (matrix) dependent. This phenomenon is known as the relative sensitivity factor (RSF). This presentation will discuss our investigations into determining accurate RSF values for U:Pu and U:Np inter-element measurements. With accurate RSF values, which should be universal for a given sample type, the measured inter-isotope ratios can be corrected to their true values. In a mixed actinide sample, there is ^{239}Pu present which will be unresolvable from $^{238}\text{U}^+\text{H}$. This will prevent a conventional hydride correction on measurements, and there are not other clean masses in a mixed actinide sample where a hydride signal can be easily measured. Without a hydride correction the measurement of smaller concentration isotopes will have poor accuracy due to interference from large hydride interferences from major isotopes, and ^{239}Pu measurements will be highly inaccurate. The presentation will discuss our use of energy filtering mediated by an intentionally introduced partial pressure of oxygen in the sample analysis chamber, which changes ionization behavior.

8:40am **AS+BI+RA-TuM3 Utilizing Large Geometry Secondary Ion Mass Spectrometry for Age-Dating of Individual Uranium Particles, Christopher Szakal, D.S. Simons, J.D. Fasset, National Institute of Standards and Technology (NIST); A.J. Fahey, Corning Inc.**

Secondary ion mass spectrometry (SIMS) is routinely utilized by the International Atomic Energy Agency (IAEA) and its global partner laboratories for the isotopic analysis of individual uranium particles as part of nuclear safeguards efforts. One additional isotopic analysis that has repeatedly been requested by the IAEA involves the development of a capability to perform single particle age-dating, which would provide information about the last time that the nuclear material was purified or enriched. Previously reported efforts in multiple countries have reported the ability to use SIMS and/or large geometry (LG)-SIMS for this purpose, but with the caveat that the measurement can only be viable if the particles are large enough, old enough, and/or enriched enough. We present a new methodology, complete with propagated uncertainties, that advances the individual uranium particle age-dating measurement to include smaller, younger, and lower enriched nuclear material than previously envisioned. Additionally, we will provide insights into utility of this measurement advance within the aims of global nuclear safeguards objectives.

9:00am **AS+BI+RA-TuM4 Peak Shape Analysis in TOF SIMS: Best Practices and Limiting Precision in Accounting for Detector Saturation, Lev Gelb, A.V. Walker, University of Texas at Dallas**

We compare strategies for analyzing high-mass resolution TOF SIMS data sets affected by detector saturation. The detectors used in many instruments undercount ions due to saturation effects. If two or more ions arrive within a very short interval (the "dead time") only the first ion is recorded. This changes both the total number of ions collected and their

statistical distribution. The dead time is typically short enough that only ions of the same nominal mass are affected, but a significant fraction of the total ions reaching the detector may still be missed.

We demonstrate an approach to correct for dead time errors in which a probability model for the detector behavior is developed and used in peak fitting of the "uncorrected" data. This approach has many advantages over previous methods which required an estimate of the variance, and it behaves better under conditions of poor data quality (low counts or high saturation.)

Using both synthetic and experimental data, we examine how saturation affects apparent peak shape, position and intensity, the effects of background on estimated peak position and shape, the dependence of peak-location precision on the total number of counts, how interference between satellite peaks is best accounted for, and the biases exhibited by different data analyses. Finally, we extend these methods to imaging data taken at high mass resolution and compare the results obtained with analyses performed at unit-mass resolution.

9:20am **AS+BI+RA-TuM5 Electronic Structure and Band Gaps of Industrially Relevant Materials Investigated by Photoelectron Spectroscopy and REELS (Reflection Electron Energy Loss Spectroscopy), Paul Mack, T.S. Nunney, Thermo Fisher Scientific, UK; H.M. Meyer III, Oak Ridge National Laboratory**

Many inorganic and organic materials have been created and evaluated for use in a diverse range of applications, such as microelectronics, solar cells and TV displays. The electronic properties of these materials can be tuned by modifying their elemental or chemical state composition. Ideally, the analyst would like to characterize both the composition and electronic properties of a given material in a single experimental run, enabling correlation between electronic properties and composition to be established.

In this work thin films of industrially relevant materials, such as polydiocetylfluorene, which is a polymer light emitting diode (PLED), and HfO_2 were analysed using a multi-modal approach. (Thermo Scientific ESCALAB Xi+ and Nexsa tools, configured with multiple surface analysis techniques, were used for the analysis.)

X-ray photoelectron spectroscopy was used to measure elemental and chemical state composition (together with some electronic information) and ultraviolet photoelectron spectroscopy was used to measure ionization potentials and the energies of the highest occupied molecular orbitals (HOMOs). Information about the band gap and lowest unoccupied levels (LUMOs), which cannot be determined with XPS or UPS, was measured with REELS. Energy level diagrams for the materials could then be constructed using the information from the complementary spectroscopic techniques.

Due to the low kinetic energy of photoelectrons generated by the ultraviolet source, UPS is a particularly surface sensitive spectroscopy. When analyzing samples stored in the atmosphere, the resulting data is typically dominated by surface adventitious carbon. This carbon needs to be removed, but with care not to damage the underlying material being studied. The use of an argon cluster ion beam for this kind of careful sample preparation was demonstrated in this work.

9:40am **AS+BI+RA-TuM6 Practical References for Low Energy Ion Scattering by Ca and F, S. Průša, T. Šikola, Brno University of Technology, Czech Republic; Hidde Brongersma, IONTOF Technologies GmbH, Germany/Eindhoven University of Technology, Eindhoven, The Netherlands, Germany**

Low-Energy Ion Scattering (LEIS) is known for its extreme surface sensitivity. It is just as well suited for the analysis of amorphous, isolating, extremely rough surfaces, as for flat single crystals. Thus LEIS is applicable to any type of sample that can be taken into vacuum. Since matrix effects are generally absent, or relatively small in LEIS, a quantitative analysis is straightforward. However, the theory to quantitatively predict the atomic sensitivities of the elements falls short. Therefore, an accurate quantification relies on well-defined reference materials. Practical references should be chemically inert, easy to clean and inexpensive. The powder of calcium fluoride, CaF_2 , has been suggested as practical reference for Ca and F [1], while the powder of calcium carbonate, CaCO_3 , has also been suggested for Ca [2].

A complication is that the composition of the outer atomic layer of a material is generally fundamentally and radically different from that of the atoms below this surface. Thus it is unlikely that the F/Ca ratio in the outer surface of CaF_2 will be 2. In fact, precisely this difference makes the LEIS

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information unique and complementary to that of analytic techniques such as XPS, Auger and (TOF-) SIMS which probe several to many atoms deep. The difference is also highly relevant, since the outer atoms of a surface largely control important processes as adhesion, catalysis, electron emission and growth

It will be shown how the F/Ca atomic ratio, the Ca and F atomic densities, as well as the roughness factors for CaF₂ and CaCO₃ have been determined.

[1] T. Gholian Avval, C.V. Cushman, P. Br uner, T. Grehl, H.H. Brongersma, M.R. Linford,

Surf. Sci. Spectra, to be published (2019)

[2] R.M. Almeida, R. Hickey, H. Jain, C.G. Pantano, J. Non-Cryst. Solids 385 (2014) 124

11:00am **AS+BI+RA-TuM10 Extreme-Ultraviolet-Assisted Atom Probe Tomography**, *Norman Sanford*, *L. Miaja Avila*, National Institute of Standards and Technology (NIST); *P. Blanchard*, National Institute of Standards and Technology (NIST); *D.R. Diercks*, *B. Gorman*, Colorado School of Mines; *A. Chiaramonti*, National Institute of Standards and Technology (NIST)

Laser-assisted atom probe tomography (L-APT) often returns compositional biases that deviate from a specimen's true chemical makeup [1]. In our L-APT studies of GaN, which utilize a 355 nm laser, we find stoichiometric composition (50% Ga, 50% N) only when the pulse fluence is roughly 2E-7 J/cm². Higher fluences return nonphysical, Ga-rich compositions; lower fluences give nonphysical N-rich compositions. L-APT of other materials, including SiO₂, exhibit similar biases. L-APT is a thermally-activated mechanism. The specimen is subjected to a strong electric field that is held just below the threshold for field evaporation of ions; evaporation is triggered by thermal transients imparted by the incident laser pulses. Motivated by the need to improve the quantitative accuracy of atom probe tomography, we explored an alternative, photoionization-triggered pathway for field evaporation by replacing the conventional laser on an L-APT tool with a pulsed, extreme-ultraviolet (EUV) source—thus realizing the XAPT [2,3]. The tabletop EUV source is an ultrafast, amplified Ti:sapphire laser driving an Ar-filled capillary waveguide. Pulsed, coherent EUV is produced via high-harmonic generation [4]. The respective characteristics of EUV pulse width, repetition rate, wavelength (energy), and fluence, incident on a specimen tip are: 10 fs, 10 kHz, 30 nm (42 eV), and 2.5E-8 J/cm². Comparative XAPT and L-APT analyses were performed on specimens of GaN and SiO₂ (amorphous fused silica). For SiO₂, L-APT returned an off-stoichiometry composition of 41% Si and 59% O; XAPT yielded 33% Si and 66% O (stoichiometry). For GaN, XAPT found 49% Ga and 51% N; L-APT yielded laser-pulse-fluence-dependent composition and returned 68% Ga and 32% N for a fluence of roughly 2E-6 J/cm²; L-APT conditions giving stoichiometric GaN appear above. The uncertainty of these measurements is 1–3 at. %. All specimens were examined at 50 K. XAPT-derived mass spectra show reduced occurrences of molecular ions and reduced “thermal tails” (persistent field emission following the laser pulse). Ongoing work for presentation at the meeting includes comparative studies of InGaN, Mg:GaN, and AlGaN. In all cases examined thus far, the XAPT approach offers measurable improvements over L-APT.

1. D. J. Larson, et al, Local Electrode Atom Probe Tomography (Springer, New York, 2013)

2. A. N. Chiaramonti, et al, MRS Advances (in press, 2019)

3. L. Miaja Avila, et al, Frontiers in Optic (FiO), Optical Society of America, Wash. DC, p. FTu5C. 3 (2018)

4. L. Miaja Avila, et al, Phys. Rev. Lett. 97, 113604 (2006)

11:20am **AS+BI+RA-TuM11 A Multi-Technique Approach for Complete Thin Film Characterisation**, *Sarah Coultas*, *J.D.P. Counsell*, *N. Gerrard*, *C.J. Blomfield*, Kratos Analytical Limited, UK; *C. Moffitt*, Kratos Analytical Limited; *T. Conard*, IMEC, Belgium

The application of thin film technology is of commercial importance across a range of industries and is commonly used to influence both the physical and chemical properties of bulk materials. Ranging in thickness from tens of Angstroms to microns, their applications are used across a broad range of disciplines including the semiconductor, biomaterial and energy harvesting industries. Herein, we provide a multi-technique investigation of layered thin film and ultra-thin film coatings using a model system for gate oxide structures. The combination of techniques allows one to build a complete picture of the chemistry of these materials and how subtle differences in chemistry and stoichiometry can influence the properties of a substrate to enhance its application specificity.

X-ray Photoelectron Spectroscopy (XPS) was used to characterize the surface chemistry of these layered thin film materials. Using monochromated Al-K α (1486.6 eV) X-rays, it was possible to gain quantitative chemical information from the uppermost 10 nm of the surface. In this study, we illustrate how angle-resolved XPS (ARXPS) can be used as a more surface sensitive approach to probe only the topmost 1-3 nm, and how one can utilize maximum entropy modelling (MEMS) to recreate a concentration depth profile from the resulting data.

In contrast to increased surface sensitivity, high energy excitation sources can be used to extend the analysis depth of a material to >15 nm. Here, we describe the use of a monochromated Ag-L α (2984.2 eV) X-rays to delve deeper into the bulk structure. In combination with ARXPS, the greater excitation energy and increased analysis depth allows one to measure elemental core levels which are not accessible using the conventional Al-K α source. In light of this, one can build a more detailed description of the structure of these thin film materials and their use in relevant applications.

11:40am **AS+BI+RA-TuM12 Polymeric Barrier Coatings for Silicone Elastomer against Diffusion of Isocyanate in Vacuum Casting Processes**, *Martin Wortmann*, *R. Petkau*, Bielefeld University of Applied Sciences, Germany; *N. Frese*, Bielefeld University, Germany; *E. Moritzer*, Paderborn University, Germany; *A. G lzh user*, Bielefeld University, Germany; *B. H usgen*, Bielefeld University of Applied Sciences, Germany

The vacuum casting process is used industrially to replicate prototypes of polyurethane (PUR). Due to the diffusion of 4,4'-methylene diphenyl diisocyanate (MDI), a PUR resin component, the silicone casting molds used in this process show a progressive degradation, which leads to the failure of the casting molds after a few casting cycles [1]. In this contribution, we present ways to protect the surface of the silicone elastomer by various thermoplastic polymer coatings. The polymers investigated were dissolved in different volatile solvents and coated on pretreated silicone surfaces. For this purpose, the compatibility of those polymer solutions with polydimethylsiloxane (PDMS) was investigated and their diffusion coefficients with respect to MDI were measured. Polymer coatings that have exhibited a high diffusion barrier have been used to drastically increase the output of the casting molds.

[1] M. Wortmann et al., *Polymer Plast Tech Eng* 57, 1524 (2018).

12:00pm **AS+BI+RA-TuM13 pARXPS Study of GeSbTe Surface Oxidation**, *Ludovic Goffart*, ST Microelectronics/LTM/CEA-LETI, France; *C. Vall e*, Laboratoire des Technologies de la Micro lectronique (LTM), France; *B. Pelissier*, LTM, Univ. Grenoble Alpes, CEA-LETI, France; *J.-P. Reynard*, *D. Benoit*, ST Microelectronics, France; *G. Navarro*, CEA-LETI, France

This work is focusing on the oxidation of the well-known GST material (Ge₂Sb₂Te₅, GST225) widely used in storage optics like CD, DVD and Blu-ray. This time, we use the GST for its electrical properties to create a non-volatile memory. The GST we use in this work is modified from the GST225 chemical composition to comply with the specifications needed in automotive applications, the most important being a good stability and cycling at high temperature environment.

This non stoichiometric GST composition leads to instability in its structure, therefore more aging and oxidation which conflict with the objectives of this new PCM cell. Added to this is some atomic segregation during crystallographic relaxation, which leads to low cycling durability of the cell and lower crystallization temperatures. To counter these effects, the GST material is doped but this makes more complex the chemical characterization of the material.

To understand and overcome these problems, different GST materials (from 225 to Ge rich) have been characterized using the pARXPS technique which is an angular resolved XPS. With this technique a very complete chemical characterization of the surface of these samples have been performed to gather useful information of atomic segregations and surface oxidation, by acquiring 8 simultaneous angles at the same time for different element windows. This is only possible by developing a complex fitting model for the large amount of spectra obtained. This model has to deal with the complex feature of the spectra obtained since some peaks were overlapping. Physical constraints are then necessary to obtain a realistic fit of the spectra. Once the model optimized, the aging of the samples have been studied by monitoring the evolution of specific XPS shapes with time. As a result, the oxidation kinetic and the thickness of the oxidized surfaces are quantified and finally a depth profile reconstruction of the different chemical bonds is performed. In addition to pARXPS, TEM-EDX analysis were performed to confirm the fitting model developed and profile depth reconstruction obtained with pARXPS technique.

Biomaterial Interfaces Division

Room A120-121 - Session BI+AS-TuM

Characterization of Biological and Biomaterial Surfaces

Moderators: Karyn Jarvis, Swinburne University of Technology, Sally McArthur, Swinburne University of Technology

8:00am BI+AS-TuM1 Characterizing Protein Fiber Structures in Solution with Vibrational Sum-Frequency Scattering Spectroscopy, *David G. Castner, P.K. Johansson*, University of Washington

Sum frequency generation vibrational spectroscopy has been developed as a powerful technique for investigating the structure of proteins at flat liquid-solution interfaces. However, many biological processes are regulated by interactions at the interface of 3D structures. Collagen forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are important for the survival, communication, migration, and proliferation of cells. Investigating protein fiber interactions is challenging, particularly under biological conditions. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals. We have applied SFS to collagen type I fiber networks self-assembled in aqueous environments. Signals were detected from the amide I band stretching vibrations (associated with the protein backbone structure) and signals from the C-H stretching and bending vibrations (associated with the protein side-chains). The angular scattering patterns for the backbone (amide I) and side-chain (C-H stretches and bends) signals are different, making the spectra dependent on the angle of detection. For randomly oriented fiber networks the amide I chiral signals are dominant in the phase-matched direction. In contrast, amide I achiral and chiral signal strengths are comparable at scattering angles above 6°. The backbone signal intensity decreases significantly as the scattering angle increases. In contrast, the side-chain signals remain high at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are probable reasons for these observations. The amide I band the spectra acquired at a scattering angle of 22 degrees provided good specificity to the surface region of the collagen fibers. This surface sensitivity was used to investigate how a dilute sodium dodecyl sulfate surfactant solution affects the spectra and scattering patterns of the SFS signals. The amide I SFS polarization ratios at a scattering angle of 22° provided insights to early changes to the collagen fiber structure. This shows the promise of SFS as an important technique for providing detailed information about the surface structure and chemistry of protein fibers, complementary to what can be obtained from other techniques such as SHG imaging or IR spectroscopy. Thus, SFS can provide a molecular level understanding of the changes to collagenous tissues during decellularization and help optimize the protocols for tissue engineered organs.

8:20am BI+AS-TuM2 Near-Ambient Pressure XPS Surface Characterisation of Bacteria and Biofilms - Model Systems and Sample Preparation, *Marit Kjaervik*, Bundesanstalt für Materialforschung und -prüfung, Germany; *P. Dietrich, A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany; *K. Schwibbert, W.E.S. Unger*, Bundesanstalt für Materialforschung und -prüfung, Germany

Bacterial samples are typically freeze dried or cryo-prepared prior to XPS analysis to allow for measurements in ultra-high vacuum (UHV). The sample environment in the near-ambient pressure (NAP) XPS instrument EnviroESCA allows for measurements in up to 15 mbar water vapor, thus, sample preparation is no longer restricted to UHV-compatible techniques.[1] For instance, biofilms grown in medium can be transferred directly from the medium to the measurements chamber, maintaining a humid environment throughout the measurements.[2] Considering the complexity of bacterial samples, sample preparation must be carefully considered in order to obtain meaningful and reproducible results.

In this talk, various strategies for sample preparation of bacteria and biofilms for NAP-XPS measurements will be discussed. Model systems of planktonic bacteria, artificial biofilms resembling the exopolysaccharide matrix and biofilms have been characterised in various conditions. The stability and homogeneity of the samples were assessed by monitoring the C1s core-level peak at different sample locations. The quality of the XP spectra is also influenced by the gas environment, which will be exemplified by core level spectra of *P. Fluorescens* acquired in air, water vapor and ultra-high vacuum.

Furthermore initial results from iodine doped model biofilms will be presented. The in-depth chemical composition profile of these model films was obtained using an argon gas cluster ion gun.

Acknowledgements

This project has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

[1] P. M. Dietrich, S. Bahr, T. Yamamoto, M. Meyer, and A. Thissen, "Chemical surface analysis on materials and devices under functional conditions – Environmental photoelectron spectroscopy as non-destructive tool for routine characterization," *J. Electron Spectros. Relat. Phenomena*, vol. 231, pp. 118–126, Feb. 2019.

[2] M. Kjaervik, K. Schwibbert, P. Dietrich, A. Thissen, and W. E. S. Unger, "Surface characterisation of *Escherichia coli* under various conditions by near-ambient pressure XPS," *Surf. Interface Anal.*, vol. 50, no. 11, pp. 996–1000, Nov. 2018.

8:40am BI+AS-TuM3 ToF-SIMS Imaging of Plant seed Interactions with Plant-growth Promoting Bacteria, *Yuchen Zhang, X.-Y. Yu*, Pacific Northwest National Laboratory

Presentation Summary:

This presentation aims to show that we have successfully used delayed image extraction in time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study the interaction between Brachypodium seed and plant growth-promoting bacteria (PGPB) for the first time.

Abstract

The use of time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a relatively unexplored in plant biology that is undergoing fast development [1]. The majority of existing research in plant biology that has utilized ToF-SIMS mostly involves the study of plant stems and leaves, and only a handful of studies apply it on the analysis of plant roots and/or seeds. Additionally, the use of Brachypodium distachyon (Brachypodium) as a model system for research has become more prominent in plant biology. Brachypodium, a C3 model, can provide more insight into the biological studies of other species including small grain crops such as wheat and barley [2], therefore it has a significant scientific impact in plant biology. To the best of our knowledge, this will be the first systematic ToF-SIMS imaging of Brachypodium. In this work, we obtained chemical mapping of the interaction of grains of Brachypodium with plant growth-promoting bacteria (PGPB) [3], namely, *Pseudomonas* and *Arthrobacter*, using ToF-SIMS. Specifically, the use of the delayed image extraction mode in ToF-SIMS provides chemical speciation of the Brachypodium seed surface and simultaneously captures the morphological features of the plant-bacteria interface. Our findings provide high resolution spatial distributions of fatty acids (e.g., palmitic acid, stearic acid, and arachidic acid) and phospholipid (e.g., cardiolipin) present on the Brachypodium seed surface. Spectral PCA results indicate that the biofilm and planktonic cells both have effects on the seed surfaces. In terms of seedling potentials, the seed brush is the most active after PGPB attachment on the biointerface.

Key words: ToF-SIMS, delayed image extraction, PGPB, Brachypodium, *Pseudomonas*, *Arthrobacter*

References:

1. Boughton, B.A., et al., Mass spectrometry imaging for plant biology: a review. *Phytochem Rev*, 2016. 15: p. 445-488.
2. Delaplace, P., et al., Influence of rhizobacterial volatiles on the root system architecture and the production and allocation of biomass in the model grass Brachypodium distachyon (L.) P. Beauv. *BMC Plant Biol*, 2015. 15: p. 195.
3. Scholthof, K.B.G., et al., Brachypodium: A Monocot Grass Model Genus for Plant Biology. *Plant Cell*, 2018. 30(8): p. 1673-1694.

9:00am BI+AS-TuM4 Visualization of Signaling Molecules in Brain Tissue by Multimodal Imaging with Matrix Assisted Laser Desorption/Ionization Mass Spectrometry and Time-of-Flight Secondary Ion Mass Spectrometry, *Matthias Lorenz, S.T. King, N. Borodinov, C.A. Steed, J. Chae, A.V. Ievlev, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Matrix Assisted Laser Desorption/Ionization (MALDI) is commonly used for the chemical imaging of biological tissue samples with mass spectrometry due to its capability to desorb and ionize large organic molecules with limited fragmentation, thus preserving a high degree of molecular information. MALDI is suitable to analyze species such as peptides and proteins, and the intact molecular ion is observable in many cases.[1] The

achievable spatial resolution using MALDI mass spectrometry imaging (MSI) is limited to about 30 μm using standard matrix compounds, primarily due to the dimensions of matrix crystals and the stability of the matrix coating.[2] Time-of-Flight (ToF) Secondary Ion Mass Spectrometry (SIMS) is another mass spectrometry based chemical imaging technique that can achieve a spatial resolution below 100 nm.[3] The chemical information obtained from ToF-SIMS analyses is, however, limited to smaller organic molecules and elemental species due to a more significant fragmentation of intramolecular bonds and decreasing ion yields with increasing molecular weight. We present here a workflow comprising the consecutive application of ToF-SIMS and MALDI-ToF-MS MSI to combine the strength of both chemical imaging techniques. Even though mass spectrometry based surface analysis techniques are inherently destructive in nature, the volumes of sample material that the two imaging techniques extract at each sampling location differs significantly ($\sim 30 \mu\text{m}$ vs. $\sim 100 \text{ nm}$ craters). This difference enables the assumption of a non-destructive nature for the ToF-SIMS imaging cycle relative to the MALDI sampling volume and spatial resolution, leaving a virtually pristine sample surface for a subsequent MALDI imaging cycle of the same sample area. We showcase the application of our workflow for the multimodal imaging of a coronal mouse brain tissue section, with automated co-registration of the two imaging data sets. We demonstrate how the MALDI mass spectral data enable to complement the high spatial resolution ToF-SIMS MSI data set with an additional degree of molecular structural information and discuss our workflow based on the visualization of signaling molecules in the mouse brain tissue.

[1] Todd, P.J.; Schaaff, T.G.; Chaurand, P.; Caprioli, R.M. *J. Mass Spectrom.* **2001**, *36*, 355–369.

[2] Yang, J.; Norris, J.L.; Caprioli, R. *J. Mass Spectrom.* **2018**, *53*, 1005–1012.

[3] Kollmer, F.; Paul, W.; Krehl, M.; Niehuis, E. *Surf. Interface Anal.* **2013**, *45*, 312–314.

9:20am BI+AS-TuM5 *In situ* Observation of Triacylglycerol (C39:0) and Acylceramide (C17) Colocalization in Lipid Droplets of Apoptotic Cells using ToF-SIMS, Shohini Sen-Britain, N. Li, G.E. Atilla-Gokcumen, J.A. Gardella Jr., State University of New York, Buffalo

The formation of phase segregated lipid droplets storing triacylglycerol containing polyunsaturated fatty acyl chains (PUFA-TAGs) during apoptosis, or programmed cell death, has been previously observed [1,2]. Polyunsaturated fatty acids are incorporated into PUFA-TAGs by diacylglycerol acyltransferases (DGATs) [1]. The acylation of ceramide by DGATs also produces acylceramide which has been found in lipid droplets as well [3]. The accumulation of ceramide and PUFA phospholipids sensitizes cells to cell death. Therefore, acylation of these molecules into phase segregated droplets is thought to have a protective effect [1,2].

Previous studies observing these acylated molecules in lipid droplets have utilized LC-MS of fractionated lipid droplets [1-3]. However, colocalization of these lipids has not been observed *in situ*. Previous imaging studies have been limited by the use of nonspecific lipid dyes, such as Nile red, in observing lipid droplets.

In this study, we have utilized metal-assisted time-of-flight secondary ion mass spectrometry (ToF-SIMS) to image the colocalization of TAG (C39:0) and acylceramide (C17) in apoptotic HCT-116 human colorectal carcinoma cells. We maintained sample preparation conditions used in previous microscopy studies by cutting out squares of cell culture plates containing lyophilized apoptotic HCT-116 cells. Imaging of lipids within the cells was accomplished by milling off the top half of the cells using a focused ion beam-scanning electron microscope (FIB-SEM). Imaging of gold sputter coated samples in negative ion mode allowed for the observation of high molecular weight secondary ions ($>1000 \text{ m/z}$) and of unique spectra of both TAG (C39:0) and AC (C17). Colocalization of endogenous TAG and AC were observed in apoptotic cells. TAG and AC fragmentations were determined by analyzing (1) gold sputter coated TAG and AC standards on cell culture plates and (2) standard additions of TAG and AC onto milled lyophilized apoptotic cells that were also gold sputter coated.

The work accomplished in this study illustrates the potential of identifying the spatial localization of large biomolecules in cells on insulating, high topography containing samples through the use of standard additions and high mass resolution, metal-assisted ToF-SIMS. The results are also the first reported *in situ* observation of TAG and AC colocalization in apoptotic cells.

[1] *Biochemistry* **2018**, *57*, 72–80

[2] *ACS Chemical Biology* **2016**, *11*, 2583–2587

[3] *Cell Metabolism* **2017**, *25*, 686–697

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9:40am BI+AS-TuM6 Customizing Decellularized Biopolymer Matrices to Serve as Cell-instructive Microenvironments: A ToF-SIMS Study, Valentina Magno, M. Nitschke, R. Zimmermann, N.R. Dennison, Leibniz Institute of Polymer Research Dresden, Germany; C. Werner, Leibniz Institute of Polymer Research Dresden, Germany, Deutschland, Germany

Decellularized extracellular matrix (ECM) preparations provide highly valuable options for the *in vitro* reconstitution of tissue-specific niches. In this approach, control over the ECM composition and structural assembly can be achieved through the modulation of cell culture conditions. We have previously demonstrated that adding ascorbic acid and using macromolecular crowding (MMC) allows for tuning the ECM deposition by human mesenchymal stem cells by boosting procollagen synthesis and enhanced complexation/deposition of soluble matrix components [Prewitz *et al. Biomaterials* **73** (2015) 60]. Combining both options, we have now explored the fabrication of a large set of cell-derived ECM variants which were analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and immunostaining. Principle component analysis (PCA) of the ToF-SIMS spectra and quantitative immunofluorescence data revealed distinct differences and trends in the complex ECM composition. The introduced methodology is validated by cell culture experiments using the decellularized matrix variants and concluded to provide a new level of control in tailoring matrix properties for tissue and organoid models (authors MN and VM contributed equally).

11:00am BI+AS-TuM10 Hierarchical Changes in Protein Structure: from Surface Influence to Cell Control, Sapun Parekh, University of Texas at Austin

INVITED

Protein structure, not just identity, is now appreciated as a critical variable that determines downstream biochemical reactivity. In biomaterials research, proteins are often coated onto materials to make them biocompatible; however, the structure of particular proteins on the material surface is often unknown or not taken into account, leading to inconsistent biological responses. The same protein on different biomaterial surfaces can take on distinct structures that can, for example, lead to differential receptor activation or stem cell differentiation into specific lineages. In this work, we demonstrate how both chemical and physical stimuli modulate protein structure and ultimately direct cell response. In the first part of this talk, I will show how graphene materials, with their unique physico-chemical properties and potential applications in tissue engineering, can strongly modulate fibronectin structure, cellular integrin binding, and stem cell differentiation. In the second part, I will show how physical forces on protein-based fibrin hydrogels can modulate protein structure, modifying enzymatic and integrin binding sites and drastically reducing platelet adhesion. The work presented here shows that physical and chemical properties of materials strongly influence protein structure and downstream biological responses, showing that biomaterial design should include considerations to control protein structure in addition to protein capture.

11:40am BI+AS-TuM12 The Role of Cr-N phases Prepared by Plasma Processes on 316L Stainless Steel and the Potential Use in Biocompatible Systems, Diana Galeano-Osorio, S. Vargas-Giraldo, C. Castano, Virginia Commonwealth University

The corrosion performance of chromium nitride (CrN) phases obtained by two different plasma-based techniques on 316L stainless steel was investigated by electrochemical testing in simulated body fluid, SBF. One method consisted of the surface treatment of 316L stainless steel by plasma nitriding. The other approach comprised the deposition of Cr-N thin film layers on 316L stainless steel substrates by reactive sputtering technique. The structural analysis of the Cr-N phases on the plasma nitrided samples by X-ray diffraction (XRD) showed an expanded austenite phase (S-Phase), while X-ray photoelectron spectroscopy (XPS) analysis revealed the presence of both the S-Phase and CrN. In the case of thin films, the XRD and XPS characterization predominantly showed a CrN phase. The different topographical characteristics of both approaches coupled with the surface energy characteristics and the electrochemical behavior in SBF provided valuable information for the potential use of these materials in biocompatible applications.

12:00pm BI+AS-TuM13 Direct Interspecies Electron Transfer (DIET) in Syntrophic Microbes, Cuiyun Yang, X.-Y. Yu, Pacific Northwest National Laboratory

Presentation Summary:

Tuesday Morning, October 22, 2019

This presentation will show our recent results of metabolic performance of direct interspecies electron transfer between syntrophic *Geobacter* species by using *in situ* liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS).

Abstract

Direct interspecies electron transfer (DIET) is deemed important and effective for electron exchange among syntrophic *Geobacter* species. DIET facilitates coupling of carbon, nitrogen, phosphorus biogeochemical cycles in the natural anaerobic environment [1]. In this presentation, *Geobacter sulfurreducens* and *Geobacter metallireducens* were employed to investigate the metabolic behavior of a syntrophic community cultured in a SALVI microfluidic reactor and analyzed by *in situ* liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS). More types of molecules that facilitate metallic-like electron conductivity pili or cellular outer-membrane cytochrome (e.g., OmcS) formation in the *Geobacter* co-culture community were observed than the planktonic cells. Characteristic peaks observed include aromatic acids m/z^+ 82 ($C_4H_6N_2^+$, histidine), 120 ($C_8H_{10}N^+$, phenylalanine), and 166 ($C_9H_{12}NO_2^+$, phenylalanine), benzene polymers m/z 93 ($C_6H_5O^+$), 94 ($C_6H_6O^+$), and 133 ($C_9H_9O^+$) in the co-cultured aggregate. The compositions of specific fatty acid also changed according to the culture condition when comparing the single population vs. co-cultured community. Abundance of water clusters were observed in this work and the water cluster differences observed among the cultured community, single population biofilms, or planktonic cells also suggest that other living activities of cells is possible, for instance, moderation of the solvation spheres when forming the aggregates due to IET and/or DIET. Alternatively, we hypothesize that proton-coupled electron transfer (PCET) may play a role in the syntrophic community besides DIET based on *in vivo* spectral comparisons. Our *in situ* molecular imaging results lead to the following conclusions: 1) interspecies electron transfer in co-cultured planktonic states may be mainly mediated by reduced molecular hydrogen; and 2) DIET in co-cultured aggregates functions via direct contact or microbial nanowire. Our findings improve the understanding of the electron transfer in syntrophic communities based on *in vivo* molecular imaging.

Key words: direct interspecies electron transfer (DIET), interspecies electron transfer, *Geobacter sulfurreducens*, *Geobacter metallireducens*, *in situ* liquid TOF-SIMS

References:

1. D.R. Lovley, et al., *Geobacter*: the microbe electric's physiology, ecology, and practical applications. Adv. Microbiol. Physiol., 59, 1-100, 2011.

Applied Surface Science Division Room A211 - Session AS+BI+CA+LS-TuA

Beyond Traditional Surface Analysis

Moderators: Michaeleen Pacholski, The Dow Chemical Company, Xiao-Ying Yu, Pacific Northwest National Laboratory

2:20pm AS+BI+CA+LS-TuA1 Nanotechnology as a Driver for Going Beyond Traditional Surface Analysis, *Olivier Renault*, CEA-LETI, France **INVITED**

In the last 10 years, the progress of analytical methods has been more and more strongly connected to the pressing needs from materials and processing developments in the nanoelectronics industry. The field of materials analysis is now expanding as more and more complementary information are needed to tailor new materials for particular applications. Time-consuming techniques in the past (e.g. ARPES) are now accessible with increasing throughput, whereas the reliability of others, such as depth profiling, is improving. Finally, techniques like HAXPES implemented in the past only at synchrotron facilities, are now entering into laboratories.

In this talk I will illustrate by a series of examples in the field of device technology this evolution of surface analysis getting beyond traditional methods, driven by technological developments.

3:00pm AS+BI+CA+LS-TuA3 Core Levels Sub-shell Photo-ionization Cross-sections of Au, Ag, Cu in the Hard X-ray Photon Energy Range of 7-26 keV, *Germán Rafael Castro*, J. Rubio Zuazo, Spanich CRG BM25-Spline Beamline at the ESRF, France

Hard X-ray Photo-electron spectroscopy (HAXPES)^[1] has been developed in the last 10-15 years as a unique tool for retrieving accurate non-destructive^[2] compositional and electronic bulk property of materials in the tens of nano-meters depth-scale with nano-meter resolution. Furthermore, the ability to tune the excitation energy in the hard X-ray regime enables tuning the sampling depth, i.e. depth profile analysis, but also enables the discrimination between bulk and surface effects, especially if combined with variable incident and exit angle.

However, an important drawback is the lack of knowledge of the photo-ionization cross-section at the HAXPES photon energy and in special for now accessible deeper core levels. Recently theoretical data has been reported^[6] concerning the photo-ionization cross sections and parameters of the photo-electron angular distribution for atomic subshells but for binding energies lower than 1.5 keV of all elements with $1 \leq Z \leq 100$ in the photon energy range 1.5–10 keV. Unfortunately, these calculations do not contain information for deep orbitals accessible in HAXPES, even more there are scarce experimental results reported for both depth core levels and hard x-ray excitation energies.^[3,4]

In the present work we will show the experimentally obtained relative sub-shell photo-ionization cross sections for 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d, 4f, 5s, 5p, 5d core levels of gold (Au), 2s, 2p, 3s, 3p, 3d, 4s, 4p, 4d core levels of silver (Ag) and 1s, 2s, 2p, 3s, 3p, 3d core levels of Cooper (Cu) in the X-ray photon energy range of 7–26 keV. In the case of Au, cross sections have been corrected with experimental obtained angular anisotropy parameter. A comparison with theoretical sub-shell photo-ionization cross sections, and angular anisotropy photo-ionization parameters^[5,6] will be also presented.

References

1. J. Rubio-Zuazo, G.R. Castro, *Nucl. Instrum. Methods Phys. Res. A*, **547**, 64-72 (2005).
2. J. Rubio-Zuazo, P. Ferrer, G.R. Castro, *J. Electron Spectrosc. Relat. Phenom.*, **180**, 27-33 (2010).
3. M. Gorgoi, F.Schäfers, S.Svensson, N.Mårtensson, " J. Electron Spectrosc. Relat. Phenom.", **190**, 153-158 (2013)
4. C. Kunz, S. Thiess, B. Cowie, T.-L. Lee, J. Zegenhagen, *Instrum. Methods Phys. Res. A*, **547**, 73-86 (2005).
5. J.H. Scofield, *J. Electron Spectrosc. Relat. Phenom.* **8** 129–137 (1976).
6. M.B. Trzhaskovskaya, and V.G. Yarzhevsky, *At. Data and Nucl. Data Tables*, **119** (2018) 99–174

4:20pm AS+BI+CA+LS-TuA7 Nanoscale Tomographic Mapping the Liquid-Solid Interface with Cryo-APT, *Daniel Perea*, D.K. Schreiber, J.E. Evans, V. Ryan, Pacific Northwest National Laboratory **INVITED**

The liquid-solid interface plays an essential role in many phenomena encountered in biological, chemical, and physical processes relevant to

both fundamental and applied science. However, study of the liquid/solid interface at the nanoscale is challenging as liquids are generally incompatible with many analytical techniques that require high to ultrahigh vacuum conditions. One strategy to probe the liquid-solid interface is to cryogenically freeze the liquid into solid form to preserve local ionic chemistry gradients and surface composition within a solid structure, making it more amenable to vacuum-based analyses such as Atom Probe Tomography (APT). However, the regular application of APT to hydrated materials is lacking due to challenges in preparing the necessary nanoscale needle-shaped specimens using a FIB-SEM and the subsequent environmentally-protected transfer of the frozen specimens to the APT instrument for analysis. In this presentation, I will discuss the development of a FIB-based site-specific liftout and attachment scheme of cryogenically cooled specimens involving a combination of redeposition and overcoating of organic and organometallic molecules. A modified commercially-available specimen suitcase shuttle device and an environmental transfer hub vacuum chamber at PNNL is used to facilitate environmentally-protected specimen transfer between the cryo FIB and the APT tool, allowing for the first time, APT analysis of a water/solid interface in 3D to reveal the complex nanoscale water-filled porous network of corroded glass. Application of this unique specimen preparation approach to biological specimens will also be discussed.

5:00pm AS+BI+CA+LS-TuA9 Characterization of Electronic Materials using Low Energy Inverse Photoemission Spectroscopy, *Benjamin Schmidt*, J.G. Newman, J.E. Mann, K. Artyushkova, L. Swartz, Physical Electronics; M. Terashima, T. Miyayama, ULVAC-PHI Inc., Japan

The development of complex electronic materials in areas such as batteries, solar cells, and flexible display panels require a detailed knowledge of the electronic band structure in order to achieve desired performance. A few of the material properties of interest are electron affinity, work function, ionization potential, and bandgap. Photoemission spectroscopic techniques such as Ultraviolet Photoelectron Spectroscopy (UPS) and Inverse Photoemission Spectroscopy (IPES) have traditionally been used to measure these values.

Organic electronic materials are growing in popularity due to lower costs of production and the ability to create interesting mechanical structures. However, they are susceptible to chemical damage with prolonged exposure to high-energy electron beams during analyses, which can affect the measured properties.

Low Energy Inverse Photoemission Spectroscopy (LEIPS) is a variant of IPES but uses an incident electron beam at lower energy than traditional IPES (< 5 eV vs. ~10 eV, respectively), making it less damaging for organic materials. In this talk, the operating principles of LEIPS will be discussed. Several material system examples will be shown, including films of C60 and copper phthalocyanine (CuPc).

5:20pm AS+BI+CA+LS-TuA10 Deconvolution of Atom Probe Tomography on Nanomaterials for Renewable Energy, *Margaret Fitzgerald*, M.J. Dzara, D.R. Diercks, Colorado School of Mines; N. Leick, S.T. Christensen, National Renewable Energy Laboratory; T. Gennett, S. Pylypenko, Colorado School of Mines

Technologies for hydrogen-based economy rely heavily on advancements in development of nano-structured materials. Nano-materials used in applications for energy conversion, storage and production have unique, desirable properties because of their intricate chemistries and morphologies, however this makes them difficult to characterize using traditional techniques. Of specific interest is elucidation of the surface properties and identification of differences between surface and bulk composition. This work features Atom Probe Tomography (APT) paired with other techniques that enable multi-scale characterization in 2D and 3D as a promising approach to create a more complete picture of the complexities of nano-structured materials.

APT is an incredibly powerful tool that has been used to render sub-nanometer-resolution, 3D reconstructions of metallic and, more recently, ceramic samples to enhance the understanding of local composition variations, such as around grain-boundaries and precipitates. This presentation outlines the procedures and considerations for expansion of APT towards analysis of nano-structured materials used for catalysis and hydrogen storage. Challenges related to both APT specimen preparation, APT analysis, and data reconstructions will be discussed. Specific considerations that will be addressed include sample pre-screening for mass spectrometry peak overlap, substrate and encapsulation material selection based on field evaporation compatibility, and prevention of sample damage for air- and beam-sensitive materials. In order to produce

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accurate 3D reconstructions of the APT data for these samples, initial assessment of a two-dimensional morphology of these materials is made using scanning transmission electron microscopy (STEM) and elemental distributions are acquired with energy dispersive x-ray spectroscopy (EDS). Surface chemistry of the sample is determined using X-ray Photoelectron Spectroscopy (XPS) in order to correlate surface chemistry between APT data and quantified XPS chemical ratios. This talk will provide evidence of cross-correlation across multiple techniques and integration of 2D and 3D data to provide a pathway for understanding these complex materials beyond traditional capabilities.

5:40pm **AS+BI+CA+LS-TuA11 Mass Spectrometric Investigation of Ion Solvation in Liquids, a Comparison of *in situ* Liquid SIMS to Regular ESI-MS, Yanyan Zhang**, Institute of Chemistry, Chinese Academy of Sciences, China; *D.R. Baer, Z.H. Zhu*, Pacific Northwest National Laboratory

Ion solvation plays very important roles in many important biological and environmental processes. Mass spectrometry (MS)-based methods have been used to investigate this topic with molecular insights. To study ion solvation, ionization processes should be as soft as possible in order to retain solvation structures. An *in situ* liquid secondary ion MS (SIMS) approach developed in our group has been recently utilized in investigations of Li ion solvation in nonaqueous solution, and it detected a series of solvated Li ions.^[1] As traditionally SIMS has long been recognized as a hard ionization process with strong damage occurring at the sputtering interface, it is very interesting to study further how soft *in situ* liquid SIMS can be. In this work, we used halide ion hydration as a model system to compare the ionization performance of the *in situ* liquid SIMS approach with regular electrospray ionization MS (ESI-MS). Results show that, although ESI has been recognized as a soft ionization method, nearly no solvated halide ions were detected by regular ESI-MS analysis, and only strong signals of salt ion clusters were seen. As a comparison, in liquid SIMS spectra, a series of obvious hydrated halide ion compositions could be observed.^[2] Our findings demonstrated that the *in situ* liquid SIMS approach is surprisingly soft, and it is expected to have very broad applications on investigation of various weak interactions and many other interesting chemical processes (e.g., the initial nucleation of nanoparticle formation) in liquid environment.

References:

[1] Zhang, Y.; Baer, D.; Zhu, Z.*, et al., "Investigation of Ion-Solvent Interactions in Non-Aqueous Electrolytes Using *in situ* Liquid SIMS", *Anal. Chem.*, **2018**, *90*, 3341–3348.

[2] Zhang, Y.; Zhu, Z.*, et al., "In Situ Liquid SIMS: A Surprisingly Soft Ionization Process for Investigation of Halide Ion Hydration", *Anal. Chem.* **2019**, published online, DOI: 10.1021/acs.analchem.8b05804.

6:00pm **AS+BI+CA+LS-TuA12 Characterizing the Thickness and Physical Properties of Nearly Ideal Zirconium Oxide Surfaces Using Ellipsometry, ESCA, Profilometry and FIB, Edward Gillman**, Naval Nuclear Laboratory

Zirconium alloys are used in nuclear reactor cores due to their small neutron scattering cross-section and corrosion resistance. Corrosion of zirconium alloys results in the formation of a protective oxide layer that the corrosion species must travel through in order to continue the corrosion process. This oxide prevents further oxidation of the metal, slowing down the reaction rate. Characterizing this important oxide film on a metal is difficult. A number of analytical techniques are used to better understand the properties and growth of this oxide film. To insure that reliable information is reported, the thickness and physical properties of zirconium oxide deposited on a single-crystal silicon wafer by magnetron sputtering has been investigated. Data obtained from Electron Spectroscopy for Chemical Analysis (ESCA), profilometry, ellipsometry and Focused Ion Beam (FIB) experiments are all self-consistent with each other. This validates the utility of these measurements for the characterization of the oxide observed on metallic surfaces.

Biomaterial Interfaces Division

Room A120-121 - Session BI+AS-TuA

Biomolecules and Biophysics and Interfaces & Flash Session

Moderators: Markus Valtiner, Vienna University of Technology, Austria, Tobias Weidner, Aarhus University, Denmark

2:20pm **BI+AS-TuA1 Electrochemical Surface Reactivity of Catechol Derivatives: Competitive Adsorption and Ion Effects, Laila Moreno Ostertag, L.L.E. Mears, D. Dworschak, M. Valtiner**, Vienna University of Technology, Austria

Catechols are molecules well known for their participation in important biological processes such as neurotransmission and bioadhesion. Their adhesive properties are of great interest for the development of biocompatible glues and coatings. In particular, L-3,4-dihydroxyphenylalanine (L-DOPA) has been found to play a defining role in the attachment of mussel feet to organic and inorganic surfaces in wet environments. Its electrochemistry has been widely studied, but the possibilities of many other catechols in this field remain largely unexplored, as is the effect of diverse ionic media in which their properties could be improved.

By using several electrochemical techniques and comparing to a well-known model system, we have obtained an understanding of the redox mechanisms involved in the interaction of these molecules at a metallic interface. Reaction parameters such as diffusion coefficients and reaction constants have been determined in different ionic media.

This fundamental insight allows us to set catechols in the context of their role within interfacial phenomena. Our approach enables the elucidation of free energies that characterize the energy landscape of adhesion processes at electrified interfaces, which can then bridge the gap between bulk electrochemistry and single-molecular surface-force analysis techniques. Full energy pathways can be drawn based on combined results and lead to a wide range of possibilities in the development of catechols for specific applications.

2:40pm **BI+AS-TuA2 Direct Observation of Lysozyme Interaction with a Curved Lipid Membrane Surface by Sum Frequency Scattering Vibrational Spectroscopy, Thaddeus Golbek**, Aarhus University, Denmark, Denmark; *H.I. Okur, S. Kulik, J. Dedic, S. Roke*, École Polytechnique Fédérale de Lausanne (EPFL), Switzerland; *T. Weidner*, Aarhus University, Denmark

Highly ordered protein aggregates play a large role in many neurodegenerative and non-neuropathic disorders including type II diabetes, Alzheimer's, Parkinson's, prion, and Huntington's disease. Even though a causative link between the formation of protein aggregates and server diseases has been established, the molecular level-details of protein aggregation and cell membrane disruption are still underdeveloped. One of the most characterized proteins that has been used to model protein aggregation is hen egg-white lysozyme. While lysozyme has been extensively studied at model surfaces, it has not been well studied on curved, more realistic, surfaces. In order to observe lysozyme at a curved surface we applied sum frequency scattering (SFS) vibrational spectroscopy to probe the interface between the protein and the curved lipid model cell membrane surface. The model cell membrane was built upon 10% 1,2-dimyristoyl-*sn*-glycero-3-phospho-(1'-*rac*-glycerol) (DMPG) and 90% 1,2-dipalmitoyl-*sn*-glycero-3-phosphocholine (DPPC) lipid nanodroplet emulsions, where the oil is *n*-hexadecane. SFS studies at the protein-lipid interface demonstrate that binding of lysozyme induces increased lipid monolayer order. An increase in acyl chain order determined by the ratio of the CH₃ symmetric and CH₂ asymmetric peak amplitudes and lipid head group orientation change from about 0° to greater than 60°, determined by the increase in phosphate head group signal, suggests that lysozyme inserts into the lipid layer causing lipid dehydration and reorientation. The amide I SFS spectrum lysozyme interacting with the model cell lipid monolayer is also studied to observe the folding and ordering of the protein. Altogether, we demonstrate the use of lipid monolayer nanodroplet emulsions as a platform to study protein membrane interactions in solution, which excludes air from the model further increasing biomimetic modeling potential using SFS.

3:00pm **BI+AS-TuA3 Iron Speciation at Aqueous Surfaces, Heather Allen**, Ohio State University **INVITED**

Ion pairing and speciation in the condensed phase and at the aqueous surface is presented for mono and multi-valent ions including iron and phosphate systems. We present new evidence of iron (III) surface

prevalence at both the water and glycerol surfaces. Understanding surface water solvation structure using polarized Raman and vibrational sum frequency generation spectroscopy are also discussed.

4:20pm BI+AS-TuA7 Identifying the Molecular Mechanisms that Mediate Cell Membrane Repair by Sum Frequency Generation Spectroscopy, T.W. Golbek, Oregon State University; S.J. Roeters, T. Weidner, Aarhus University, Denmark; C.P. Johnson, Joe Baio, Oregon State University

Movement in everyday life places stress on sarcolemma which creates small tears in the muscle cell membrane. Mutations in this multi-domain dysferlin protein render it unable to repair the membrane and this phenomena is related to diseases such as specific forms of muscular dystrophy. Of particular importance is the moment after the release of calcium from tears in the muscle cell membrane, whereby the release of calcium triggers the C2A domain of dysferlin to dock with a lipid vesicle. Mutations mapped to this domain cause loss of binding ability of the C2A domain. This is the first step of muscle cell membrane repair, therefore there is a crucial need to understand the geometry of dysferlin C2A at a membrane interface as well as cell membrane lipid reorientation when compared to a variant. Here we describe a comparison between the wild type dysferlin C2A and a mutation to the conserved aspartic acids on the domains binding loops. To identify both the geometry and the cell membrane lipid reorientation, we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the interaction. A model cell membrane was built with phosphatidylserine and phosphatidylcholine. Observed changes in surface pressure demonstrate that calcium bridged electrostatic interactions govern the initial interaction of the C2A domains docking with a lipid membrane. SFG spectra taken from the amide I region for wild type and variant contain features near 1642 cm^{-1} , 1663 cm^{-1} , and 1675 cm^{-1} related to the C2A domains beta-sandwich secondary structure indicates that the domain binds in a specific orientation. Mapping simulated SFG spectra to the experimentally collected spectra indicated that both wild type and variant domains have nearly the same orientation to the membrane surface. However, examining the ordering of the lipids that make up a model membrane using SFG, we find that the wild type clusters the lipids as seen by the ratio of the CD3 and CD2 symmetric intensities increases by 170% for the wild type and by 120% for the variant. This study demonstrates and highlights the capabilities of SFG to probe with great detail biological mutations in proteins at cell membrane interfaces.

4:40pm BI+AS-TuA8 Fishing Manganese out from Cellulose: Impact of Coupling Desferrioxamine B to Stainless Steel Beads on the Circular Economy of Paper and Pulp Industry, Jeff Wilkesman¹, Mannheim University of Applied Sciences, Germany; K. Mörzter, I. Sommer, P.M. Kunz, Mannheim University of Applied Sciences, Deutschland

Important as an essential trace element with abundant applications, manganese (Mn) is rising attention due to its aesthetic, operational and health problems at higher concentration in the paper and water industry. When oxygen-containing paper bleaching chemicals (O_2 , O_3 , H_2O_2 or peracids) are used, the presence of heavy metals like Mn causes problems in the pulp processing, increasing the consumption of the bleaching chemicals and deteriorating pulp quality, including pulp darkening. An effective way to remove Mn from pulp is employing chelators, although its effectiveness is influenced by the overall water chemistry and concomitant contaminants. Successful chelation of Mn usually occurs at $\text{pH} < 8$, otherwise highly oxidized species would form, precipitating insoluble Mn(III/IV) oxide minerals, and binding strongly to the pulp. Though the environmentally critical EDTA is used in the paper industry to chelate heavy metals, friendlier and greener alternatives are sought, like desferrioxamine B (DFOB) or E (DFOE), which are linear trihydroxamic acid siderophores produced by bacteria to acquire primarily Fe(III), but also Mn(II/III). Advantages of employing siderophores are its commercial availability, high solubility and stability over a wide pH range. The coupling of DFOB to ~3-4 mm stainless steel beads as solid support was performed. The beads were incubated overnight with several cellulose suspensions to allow formation of the Mn-DFOB complex ($\log K \sim 29.9$). Control assays were performed using EDTA. After treatment, cellulose suspensions originally containing ~30-40 mg Mn/kg, were submitted for Mn(II), Mn(III) analysis, employing the TCPPP [Tetrakis(4-carboxyphenyl)porphyrin] method. Total Mn content was also determined by Inductively Coupled Plasma (ICP). Preliminary results show an approximate 80% reduction of Mn content from the cellulose suspension, though experimentation is still carried on; DFOE is planned to be also analyzed. Mn was recovered by decoupling from DFOB

by metal exchange and the beads were reused for further activation with DFOB. This removal alternative resulted in a feasible, easy, greener and economical procedure, leading for improvement in the paper industry. Still, the most expedient option comprising circular economy statements based on sustainable management parameters (cost-effectiveness, performance, simplicity) must be deeper explored. Clearly, further research regarding Mn(II/III) formation and removal will help the water and paper industry, by developing better methods to diminish Mn oxide deposits in pipe networks and optimizing the paper bleaching process, ultimately reducing significant operational costs.

5:00pm BI+AS-TuA9 The Hybrid Nano-biointerfaces Between Gold, Graphene Oxide and Angiogenin for Wound Repair, Diego La Mendola, University of Pisa, Italy; L.M. Cucci, G. Villaggio, C. Satriano, University of Catania, Italy

Angiogenin (ANG) is a member of the ribonuclease family and a physiological constituent of the human plasma. Ang is a potent angiogenic factor regulating a wide range of responses, such as angiogenesis, cell proliferation, cell migration, and pro-survival effects. ANG has been shown related to many pathophysiological processes, including cancers, neurodegeneration, inflammation and regeneration of damaged tissues. In this work, we investigated a hybrid obtained by the assembly of ANG to gold nanoparticles and graphene oxide nanosheets, to exploit the synergic effects of antioxidant AuNP and antimicrobial GO, respectively. Au-GO-ANG were characterized by UV-visible spectroscopy, to correlate the changes in the plasmonic peak as well as in the $\pi \rightarrow \pi^*$ transitions to the protein interaction with Au and GO, respectively. QCM-D measurements on supported lipid bilayers, as model of cell membranes, pointed to a stronger interaction of the AuNP-Ang systems in comparison with the uncoated nanoparticles. The developed systems promoted fibroblasts migration and wound closure. Confocal microscopy cell imaging evidenced dynamic processes at the level of cytoskeleton and sub-cellular compartments. The results reveal a promising multifunctional platform for wound care treatment and tissue regeneration.

5:20pm BI+AS-TuA10 Improved Antibacterial Sandwich system for Urological Purposes, Sara Bröskamp, G. Franz, Munich University of Applied Sciences, Germany; D. Jocham, University Hospital of Schleswig-Holstein, Germany

In the anaerobic environment of kidneys and bladder which even lack the permanent presence of weak but always toxic oxidative reagents (like ClO_2^-) it is obvious that no Ag^+ ions can be generated by oxidation of a metallic silver film. However, it is well known that the antibacterial impact of Ag^+ ions which can act as a single ion is much higher than the effect of neutral silver nanoparticles [1]. In our efforts to define an effective membrane which is deposited on the interior and exterior surfaces of tubes which exhibit an aspect ratio of more than 100 (balloon catheters) we introduce a significantly improved coating which makes use of the soft oxidation of already deposited silver layers by a microwave or RF plasma [2]. This procedure not only improves the antibacterial effect but also extends the active time of the catheters. The silver oxide on top of the base silver layer which is deposited on an originally hydrophobic surface of an organic polymer by a well-known process is eventually topped by an organic layer of comparable thickness [3,4]. This coating with even thickness on the interior of the tubes has been extensively improved by a device which counteracts the decreasing vapor density of the film-building species by a well-defined temperature gradient [5]. In the case of ureteral stents, we make use of the series of drainage holes along the catheter which act as adjacent sources for the film-building monomer. This layer controls the antibacterial activity which can be effectively tuned by its porosity [6]. The oxidation of the silver also effectively prevents sulfidation by S-containing amino acids (cysteine) which can be present in the kidneys of patients. The silver release rate has been measured by atomic absorption spectroscopy (AAS).

[1] Heidari Zare, V. Juhart, A. Vass, G. Franz, and D. Jocham; *Biointerphases* 12, 011001 (2017).

[2] G. Franz, S. Bröskamp, K. Resch, W. Hiemeyer, D. Jocham; German patent disclosure DE 10 2019 001 994.6, Mar 26, 2019.

[3] G. Franz, F. Schamberger, A. Kutschera, S. Seyedi, D. Jocham, German patent disclosure DE 102012023349.3, Nov. 29, 2012.

[4] G. Franz, F. Schamberger, H. Heidari Zare, S.F. Bröskamp, and D. Jocham; *Beilstein J. Nanotechnol.* 8, 1982 (2017). [5] S. Bröskamp, D. Redka, A. Möhlmann, G. Franz, and D. Jocham; *AIP Advances* 7, 075005(2017).

[6] F. Schamberger, A. Ziegler, and G. Franz, *J. Vac. Sci. Technol. B* 30, 01801 (2012).

5:40pm **BI+AS-TuA11 Quantitative Characterization of Piezoelectric Property in Biological System via Piezoresponse Force Microscopy**, *Jinha Kwon, D.G. Kim, H. Cho*, The Ohio State University

Piezoresponse force microscopy (PFM) is a variant of scanning probe microscopic technique based on atomic force microscopy (AFM) that allows imaging of piezoelectric material domains with high resolution. This is achieved by keeping a sharp conductive probe in contact with a piezoelectric material and applying an alternating current (AC) directly to the sample through the probe, which results in deflection of the probe detected through photodiode detector. PFM has been successfully applied to many biological materials such as teeth [1], bone [2], seashell [3], and collagen fibrils [4]. Although biological samples are commonly vulnerable to high voltage input, previous studies used a high voltage input more than 10V to induce a piezoelectric strain large enough to be captured by an AFM tip [5]. Moreover, previous works did not carefully scrutinize the effect of substrate's conductivity and the contribution of parasitic electrostatic forces between the tip and sample, which should be precisely examined to obtain the quantitative piezoelectric properties of sample. In this study, we used type I collagen fibril which has weak piezoelectricity around 1 pm/V. The collagen fibril was aligned to the probe perpendicularly and AC voltage was applied to the fibril through the conductive AFM tip which was carefully calibrated in both vertical and lateral directions. In order to amplify its piezoresponse signal with a small electrical input, we utilized the contact resonance of an AFM cantilever. We also carefully examined the effect of substrate's conductivity by comparing piezoelectric response of the collagen on bare and gold-coated glass slides. Moreover, the contribution of electrostatic forces to the PFM results were investigated while they are varied by applying different DC offsets simultaneously to compensate the electrostatic force. Finally, the piezoelectric property of the collagen was calculated by fitting the measured piezoresponse vs. applied voltage graph. As a result, the piezoelectric properties of a single collagen fibril were precisely characterized in both vertical and shear directions and its heterogeneous nature within a fibril was revealed.

[1] S.V. Kalinin, B.J. Rodriguez, J. Shin, S. Jesse, V. Grichko, T. Thundat, A.P. Baddorf, A. Gruverman, *Bioelectromechanical imaging by scanning probe microscopy: Galvani's experiment at the nanoscale*, *Ultramicroscopy*. 106 (2006) 334–340.

[2] M. Minary-Jolandan, M.-F. Yu, *Shear piezoelectricity in bone at the nanoscale*, *Appl. Phys. Lett.* 97 (2010) 153127.

[3] T. Li, K. Zeng, *Nanoscale piezoelectric and ferroelectric behaviors of seashell by piezoresponse force microscopy*, *J. Appl. Phys.* 113 (2013) 187202.

[4] M. Minary-Jolandan, M.-F. Yu, *Nanoscale characterization of isolated individual type I collagen fibrils: polarization and piezoelectricity*, *Nanotechnology*. 20 (2009) 085706.

[5] D. Denning, J.I. Kilpatrick, E. Fukada, N. Zhang, S. Habelitz, A. Fertala, M.D. Gilchrist, Y. Zhang, S.A.M. Tofail, B.J. Rodriguez, *Piezoelectric Tensor of Collagen Fibrils Determined at the Nanoscale*, *ACS Biomater. Sci. Eng.* 3 (2017) 929–935.

Biomaterial Interfaces Division

Room Union Station B - Session BI-TuP

Biomaterial Interfaces Posters/Flash Session

BI-TuP1 Combining Geometry of Folded Paper with Liquid-Infused Polymer Surfaces to Concentrate and Localize Complex Solutions, Daniel Regan, C. Lilly, A. Weigang, L. White, E. LeClair, C. Howell, University of Maine

Diagnostic devices which can provide information relevant to health and safety on-site without the requirement for a fully-equipped laboratory are of great interest for medical, military, and disaster relief applications. However, most research and development work on such devices focuses on detection rather than the preliminary sample handling and preparation. In this work, we demonstrate how low-cost paper materials coated with liquid-infused polymer surfaces can be fabricated and folded to produce shapes which result in functional sample preparation; namely, the simultaneous localization and concentration of a liquid sample. Surfaces were fabricated by infusing commercially-available silicone-release paper with a compatible polydimethylsiloxane oil to create a liquid overlayer. Adhesion tests with *Escherichia coli* on these surfaces showed no remaining bacterial cells after exposure to a sliding droplet containing 10^8 cells/mL, compared to the macro- and micro-scale bacterial residues remaining on the controls. Folding of the paper substrates into several 3D engineered arrays enabled clean separation of dye-containing liquids into discreet, pre-defined localized points, whereas the use of unfused controls resulted in the retention of dye on the sides. When used with a bacterial solution, the combined features of low bacterial adhesion and liquid separation via geometry resulted in the localization of a solution of *E. coli* and simultaneous concentration by 23.1 (± 6.5) times, compared to only 6.78 (± 3.6) times for unfused controls ($P=0.004$). This work demonstrates the potential of paper-based materials with liquid-infused polymer surfaces for the manipulation and handling of complex samples which may help in the future design of on-site diagnostics.

BI-TuP2 Photoinduced Amphiphilic Zwitterionic Carboxybetaine Polymer Coatings with Marine Antifouling Properties, Florian Victor Koschitzki, A. Rosenhahn, Ruhr-University Bochum, Germany

Due to ecological and economic consequences, the prevention of undesirable settlement of biomass on surfaces in the marine environment is of key interest. Thus, research on effective surface-modification and application of antifouling coatings is demanded. Zwitterion containing hydrogels with stable hydration have shown promising results for ultra-low fouling materials. The spectrum of application ranges from protein and plasma resistance¹, studies of bacterial adhesion², biomedical purposes³ to settlement experiments with marine biofoulers.⁴ Although understanding the influence of anionic and cationic groups, charge distribution and charge neutrality can be discussed using self-assembled monolayers⁵ (SAM), zwitterionic moieties must eventually be applied in the form of polymer coatings for technical purposes. To combine mechanical and antifouling properties of several materials, amphiphilic polymers are increasingly being explored.⁶ To demonstrate the advantage of random copolymers over homopolymers regarding antifouling⁷, polymer coatings with varying hydrophilicity were prepared. Therefore, a carboxybetaine methacrylate was incorporated into a hydrophobic matrix via «grafting to» photoinduced radical polymerisation. Monomer solutions were applied on glass substrates, functionalized by 3-trimethoxysilyl propyl methacrylate. The samples were characterized by AFM, CA, IR and SEM. For further investigations concerning the antifouling properties, microfluidic experiments with the diatom genus *Navicula perminuta* were carried out. The results display severe enhancement of fouling prevention at small zwitterionic content of only (5 wt%).

[1] – W. Yang, H. Xue, W. Li, J. Zhang, S. Jiang, *Langmuir* **2009**, *25*, 11911-11916.

[2] – G. Cheng, G. Z. Li, H. Xue, S. F. Chen, J. D. Bryers, S. Y. Jiang, *Biomaterials* **2009**, *30*, 5234-5240.

[3] – L. Zhang, Z. Cao, T. Bai, L. Carr, J.-R. Ella-Menye, C. Irvin, B. D. Ratner, S. Jiang, *Nat Biotech* **2013**, *31*, 553-556.

[4] – S. Y. Jiang, Z. Cao, *Advanced Materials* **2009**, *21*, 1-13.

[5] – S. Bauer, J.A. Finlay, I. Thome, K. Nolte, S. C. Franco, E. Ralston, G. E. Swain, A. S. Clare, and A.

Rosenhahn, *Langmuir* **2016**, *32*, 5663.

[6] – C. Ventura, A. J. Guerin, O. El-Zubir, A. J. Ruiz-Sanchez, L. I. Dixon, K. J. Reynolds, M. L. Dale, J. Ferguson, A. Houlton, B. R. Horrocks, A. S. Clare, D. A. Fulton, *Biofouling* **2017**, *33*, 892-903.

[7] – A. L. Hook, C.-Y. Chang, J. Yang, J. Luckett, A. Cockayne, S. Atkinson, Y. Mei, R. Bayston, D.J. Irvine, R. Langer *et al.*, *Nature biotechnology* **2012**, *30*, 868.

BI-TuP3 Peptide sequences with Ultra-Low Nonspecific Protein Adsorption and Resistance Against Marine Biofouling, Cindy Denise Beyer, M. Reback, Ruhr-University Bochum, Germany; J.A. Finlay, Newcastle University, UK; S. Gopal, Ruhr-University Bochum, Germany; A.S. Clare, Newcastle University, UK; L. Schäfer, N. Metzler-Nolte, A. Rosenhahn, Ruhr-University Bochum, Germany

Efficient fouling-release coatings frequently consist of a silicone network modified by additional chemical compounds that reduce adhesion of marine fouling organisms. We explored the fouling-release potential of several oligopeptide sequences and tested them as self-assembled monolayers. The design motif of the peptide sequences considered inherent properties such as conformation and hydrophilicity. Different sequences were synthesized, and well-hydrated peptide coatings were assembled. All surfaces were characterized with respect to their wettability, layer thickness, and surface structure by contact angle goniometry, spectroscopic ellipsometry, and FTIR-spectroscopy. Protein adsorption of fibrinogen and lysozyme was very low on the oligopeptide SAMs. The assembled monolayers show remarkable fouling-release behavior against *Navicula perminuta* which was tested in a microfluidic assay. Also, the settlement of zoospores of the green algae *Ulva linza* was investigated. Besides the good antifouling behavior, the inclusion of Aib and D amino acids helped to create peptides that were 100% resistant against enzymatic degradation by trypsin. Due to their diversity, easy synthesis and biocompatibility, peptides could be used as active, hydrophilic components in fouling-release technologies.

BI-TuP4 The Effect of Surface Charge and Film Hydration on the Antifouling Performance of Polyelectrolyte Multilayers, Thuvarakhan Gnanasampanthan, Ruhr University Bochum, Germany; A. Rosenhahn, Ruhr-University Bochum, Germany

Marine biofouling, which describes the accumulation of animals, plants, and microorganisms on surfaces in the aqueous environment, causes tremendous economic and ecological concerns.^{[1][2]} Since commonly used antifouling coatings were banned and restricted because of their toxicity, new non-toxic alternatives must be developed and established.^[3] Polyelectrolyte multilayers are widely applied when protein resistance^[4] and antibacterial properties^[5] are required and provide a suitable platform to test the antifouling capabilities of promising compounds such as alginate acid (AA)^[6], chitosan (CH)^[7] and polyethylenimine (PEI)^[8]. The physicochemical and marine antifouling properties of chemically cross-linked alginate acid/chitosan- and alginate acid/polyethylenimine-multilayers where investigated with a focus on the influence of surface charge and film hydration. Surface plasmon resonance spectroscopy revealed that all multilayers exhibit high protein resistance. Both, positively and negatively terminated AA/PEI-multilayers did not show any differences regarding the amount of irreversibly bound protein, neither for negatively charged nor for positively charged proteins. However, for the AA/CH-coatings the charge of the terminating layer had an effect on the protein adsorption. Besides, the type of polymer within the multilayers had a strong influence on the protein resistance. Microfluidic diatom accumulation assays^[9] demonstrated that all multilayers present relatively low diatom settlement and that especially for AA/PEI-multilayers the charge of the terminating layer has a significant influence on the attachment.

References

[1] M. P. Schultz, *Biofouling* **2007**, *23*, 331.

[2] I. B. Beech, J. Sunner, *Curr. Opin. Biotechnol.* **2004**, *15*, 181.

[3] D. M. Yebra, S. Kiil, K. Dam-Johansen, *Prog. Org. Coat.* **2004**, *50*, 75.

[4] J. H. H. Bongaerts, J. J. Cooper-White, J. R. Stokes, *Biomacromolecules* **2009**, *10*, 1287.

[5] P.-H. Chua, K.-G. Neoh, E.-T. Kang, W. Wang, *Biomaterials* **2008**, *29*, 1412.

[6] Y. Li, J. Rodrigues, H. Tomás, *Chemical Society reviews* **2012**, *41*, 2193.

[7] O. Yemul, T. Imae, *Colloid Polym Sci* **2008**, *286*, 747.

[8] M. N.V. Ravi Kumar, *React. Funct. Polym.* **2000**, *46*, 1.

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[9] K. A. Nolte, J. Schwarze, C. D. Beyer, O. Özcan, A. Rosenhahn, *Biointerphases* **2018**, *13*, 41007.

BI-TuP5 Mass Spectrometric Determination of Active Adsorption sites of soil organic Carbon on Clay Mineral Surface, Zihua Zhu, L. Huang, Pacific Northwest National Laboratory; *W. Liu*, China University of Geosciences, Wuhan

The heterogenic active adsorption sites on mineral surfaces may harbor critical determination on the protecting capability, preference and efficiency on soil organic carbon (SOC) components. Molecular evidence to show organic behaviors during mineral-microbe-organic interactions is urgently needed to reveal the underlying protecting-releasing mechanism for better prediction on the SOC dynamics. However, such information has been hard to obtain in the complex soil systems. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis tool with unique advantages to reveal systematical changes of both SOC and mineral surfaces during mineral-microbe-organic interactions. In this work, ToF-SIMS and principle component analysis (PCA) were used to study the molecular mechanisms of organic preference (e.g., humic substances vs. microbial carbon) by Fe-rich clay mineral (e.g., nontronite NAu-2) during microbial Fe redox processes. Active adsorption sites, which have only been hypothesized or computationally investigated in previous research, were successfully determined by ToF-SIMS data. Such a success indicates a bright future of extensive application of ToF-SIMS and PCA on this field.

BI-TuP6 Blood Compatible Coating using Tethered Heparin to Reduce Coagulation in Microfluidic Devices, Ryan Faase, W. Prusinski, KS. Schilke, A. Higgins, J.E. Baio, Oregon State University

Hyperbilirubinemia, a condition characterized by excessive bilirubin levels, affects over half of newborn babies and can lead to serious complications including brain damage or death. Absorption of light by bilirubin leads to isomerization reactions that convert bilirubin into more readily excreted compounds (e.g. lumirubin). Here, an extracorporeal microfluidic device has been developed and optimized to isomerize bilirubin in neonates, with an efficiency that exceeds the current treatment, exchange blood transfusions. The microfluidic devices are formed from cyclic olefin copolymer and the main design challenge for this device is hemocompatibility. Our approach is to modify the blood contacting channels by tethering heparin, a powerful anti-coagulant, to the surface. This is achieved by first coating the surfaces with poly(dopamine) (PDA) and then adsorbing silver nanoparticles onto the PDA layer followed by a thiol based amine terminated self-assembled monolayer (SAM). PDA provides a route for coating virtually any surface and along with silver nanoparticles the PDA-silver interface becomes antimicrobial. The SAM formed on the PDA-silver surface can be tailored for covalent linkage of the desired molecule. For this device, heparin is chemically modified, while retaining the active site, and covalently attached to the SAM with an end-on orientation to preserve activity. Heparin's potency, in terms of anti-coagulative power, comes from a heavily sulfated penta-saccharide sequence. This sequence selectively binds precursors that produce fibrinogen, the basis of a clot. Therefore, the heparin must be covalently bound in an end-on orientation to expose this penta-saccharide sequence as opposed to allowing it to adsorb to the surface. Fluorescent microscopy provides the relative coverage of available sites for heparin attachment. Fluorescein isothiocyanate is selective to primary amines and demonstrate the density of amines that can be covalently bonded with heparin. Additionally, surface density of these amine groups was confirmed by X-ray photoelectron spectroscopy. Finally, the activity of surface bound heparin is dependent on orientation with respect to the channel surface. Thus, sum frequency generation vibrational spectroscopy provides information on the tilt angle of heparin at an interface by probing S=O, C-H and O-H vibrational modes at the modified surface.

BI-TuP7 Analysing the Sequestration of Pro-inflammatory Chemokines into Immuno-modulating Hydrogels using ToF SIMS, Nicholas Dennison, R. Zimmermann, M. Nitschke, V. Magno, U. Freudenberg, C. Werner, Leibniz Institute of Polymer Research Dresden, Germany

Chemokines are a class of signalling molecules that play a crucial role in the wound healing process by recruiting immune cells to the affected tissue. In chronic inflammations, this physiological response is prolonged and exacerbated, ultimately causing the destruction of the inflamed tissue and, consequently, the production of more pro-inflammatory chemokines.

One way of interrupting this vicious cycle of chronic inflammations is to remove chemokines from the tissue. Our group has previously demonstrated that hydrogels based on star-shaped polyethylene glycol (starPEG) and desulfated heparin show a promising sequestration pattern

of pro-inflammatory chemokines including interleukin-8 (IL-8) and macrophage inflammatory protein-1a (MCP-1) [Lohmann et al. *Sci. Transl. Med.* **9** (2017)].

Analysis of chemokine-loaded hydrogels with time-of-flight secondary ion mass spectrometry (ToF-SIMS) and principle component analysis (PCA) of the obtained spectra allowed for further characterisation of the scavenging process. The results obtained through this methodology were integrated with the enzyme-linked immunosorbent assay (ELISA) detection technique to further optimise the immune-modulating hydrogel.

Atomic Scale Processing Focus Topic Room B130 - Session AP+BI+PS+TF-WeM

Surface Reaction Analysis and Emerging Applications of Atomic Scale Processing

Moderator: Eric A. Joseph, IBM T.J. Watson Research Center

8:00am **AP+BI+PS+TF-WeM1 Open Spaces in Al₂O₃ Film Deposited on Widegap Semiconductors Probed by Monoenergetic Positron Beams, Akira Uedono**, University of Tsukuba, Japan; *T. Nabatame*, NIMS, Japan; *W. Egger*, *T. Koschine*, Universität der Bundeswehr München, Germany; *C. Hugenschmidt*, *M. Dickmann*, Technische Universität München, Germany; *M. Sumiya*, NIMS, Japan; *S. Ishibashi*, AIST, Japan

INVITED

Positron annihilation is a useful technique for characterizing vacancy-type defects in semiconductors, and it has been successfully used to detect defects in GaN. This technique is also useful for detecting open spaces in thin amorphous films deposited on semiconductor substrates. When a positron is implanted into condensed matter, it annihilates with an electron and emits two 511-keV gamma quanta. The energy distribution of the annihilation gamma rays is broadened by the momentum component of the annihilating electron-positron pair. A freely diffusing positron may be localized in a vacancy-type defect because of Coulomb repulsion from positively charged ion cores. Because the momentum distribution of the electrons in such defects differs from that of electrons in the bulk material, these defects can be detected by measuring the Doppler broadening spectra of the annihilation radiation. Because the electron density in open spaces or vacancy-type defects is lower than that in the bulk, the lifetime of positrons trapped by such regions is longer than that of positrons in the delocalized state. Thus, the measurement of the positron lifetime also provides information of open spaces and vacancies in solid. In the present work, open spaces and defects in the Al₂O₃(25 nm)/GaN structure were probed by using monoenergetic positron beams.

Al₂O₃ films were deposited on GaN by atomic layer deposition at 300°C. Temperature treatment above 800°C leads to the introduction of vacancy-type defects in GaN due to outdiffusion of atoms from GaN into Al₂O₃. The width of the damaged region was determined to be 40-50 nm from the Al₂O₃/GaN interface, and some of the vacancies were identified to act as electron trapping centers. In the Al₂O₃ film before and after annealing treatment at 300-900°C, open spaces with three different sizes were found to coexist. The density of medium-sized open spaces started to decrease above 800°C, which was associated with the interaction between GaN and Al₂O₃. Effects of the electron trapping/detrapping processes of interface states on the flat band voltage and the defects in GaN were also discussed.

The present research suggests that the interaction between amorphous Al₂O₃ and GaN introduces not only vacancy-type defects in GaN but also changes the matrix structure of Al₂O₃ film. We also revealed that the electron trapping/detrapping processes of interface charge states are influenced by the defects introduced in GaN.

8:40am **AP+BI+PS+TF-WeM3 Surface Reaction Analyses of Atomic-layer Etching by Controlled Beam Experiments, Kazuhiro Karahashi, T. Ito, S. Hamaguchi**, Osaka University, Japan

In manufacturing of modern advanced semiconductor devices such as magnetoresistive random-access memories (MRAMs), phase-change random-access memories (PRAMs), and three-dimensional integrated circuit (3D IC) devices, damage-free high-precision etching for various materials is an indispensable process technology. Halogenation of a surface layer combined with low-energy ion bombardment or ligand-exchange of organic molecules for the formation of metal complexes is a surface reaction that may be used for such highly selective etching processes with atomic-scale precision. A better understanding of surface reactions taking place during the etching process often allows one to control and optimize the process more effectively. In this study, we have developed a new surface-reaction analysis system with highly controlled beams of various species and examined surface reaction mechanisms of plasma-assisted or thermal atomic-layer etching (ALE) processes for silicon (Si), copper (Cu), and nickel (Ni) films. The beam experiment of this system offers an experimental "simulation" of actual ALE surface reactions. The system is equipped with differentially-pumped multiple beam sources that can irradiate the sample set in an ultra-high-vacuum (UHV) chamber with different types of beams, i.e., low-energy ions, thermal molecules, metastable radicals, and atomic/molecular clusters, independently. During the beam irradiation, scattered and desorbed species may be measured by

a differentially pumped quadrupole mass spectrometer (QMS). Time-resolved measurements of QMS synchronized with pulsed beam irradiation facilitate detailed analysis of the beam-surface interactions. Chemical states of adsorbed species on the sample surface may be measured by X-ray photoelectron spectroscopy (XPS). In this presentation, we discuss the mechanisms of halogenated-layer formation on the Si, Cu, or Ni surfaces by their exposure to XeF₂ or Cl₂ gases and the removal mechanisms of halogenated species from the surface by low-energy ion irradiation or surface heating. Thermal desorption mechanisms of Cu or Ni by the metal-complex formation with organic molecules (such as diketones) from its oxidized surface are also discussed.

9:00am **AP+BI+PS+TF-WeM4 Surface Reaction Analysis of Fluorine-based Reactive Ion Etching (RIE) and Atomic Layer Etching (ALE) by Molecular Dynamics (MD) Simulation, Erin Joy Tinacba, M. Isobe, K. Karahashi, S. Hamaguchi**, Osaka University, Japan

Plasma etching has always been a useful process in semiconductor device fabrication. There are several ways of using plasma etching such as reactive ion etching (RIE), wherein the material surface is bombarded with energetic ions while it also exposed to chemically reactive radicals from the plasma. Because of the energy provided by bombarding ions and high chemical reactivity on the surface, the surface is etched even at a relatively low temperature due to the combination of physical and chemical sputtering effects. RIE is often suited to fast etching processes of high aspect ratio structures since it can provide high etching yields. Another application of plasma etching is plasma-assisted atomic layer etching (ALE), wherein chemical and sputtering effects of typical plasma etching are separated into two steps. In a typical ALE process, the first step is an adsorption step wherein chemically reactive molecules or radicals from a plasma are used to modify the material surface. The modified monolayer or a thin layer on the material surface is then etched during the subsequent desorption step (second step) where low-energy ions bombard the surface. The etching reaction stops when the modified layer is depleted. This cycle is repeated many times until the desired etched depth is reached. The ALE process might be slow but it can provide tight control in the etch variability for sub-10 nm technology applications.

In this paper, molecular dynamic (MD) simulation is used to understand the effects of ions and radicals of high fluorine (F) content on etching reactions of silicon (Si), silicon dioxide (SiO₂), and silicon nitride (Si₃N₄), which may be observed in RIE processes based on, e.g., SF₆, C₂F₆, or NF₃ plasmas. If such a plasma is used as a radical source and ion bombardment steps by inert gas ions are separated from the radical exposure steps, an ALE process may be performed with similar surface reactions. In typical RIE, a supply of a large amount of fluorine to the surface by increasing the flux of energetic ions containing multiple F atoms (such as SF₅⁺, C₂F₅⁺ and NF₂⁺ ions) and/or by increasing a F radical flux to the surface results in high etch rates. It has been found that the etching rates by such highly fluorinated ions obtained from MD simulations are in good agreement with experimental observations and the deep fluorination of the surface accounts for their high etch rates. Although fluorine may be considered too corrosive to be used for ALE, we also analyzed by MD simulation an ALE process by fluorine-containing radicals such as NF₂ and compared the results with experimental observations.

9:20am **AP+BI+PS+TF-WeM5 Analysis of Metal Surface during Atomic Layer Etching with Gas Cluster Ion Beam and Organic Acid, Noriaki Toyoda, K. Uematsu**, University of Hyogo, Japan

Surface states of metal surface after atomic layer etchings (ALE) with gas cluster ion beam (GCIB) and organic acid were investigated using surface analysis tools (mainly X-ray photoelectron microscopy). In recent years, we have reported the usage of GCIB irradiation for the removal steps of ALE. Since GCIBs are aggregates of thousands of gas atoms or molecules, the energy/atoms or energy/molecules can be easily reduced to several eV even though the total energy of GCIB is several keV. This characteristic is beneficial for low-damage irradiation. In additions, since GCIBs induce dense energy deposition, the bombarded area experiences transient high-temperature and high-pressure conditions. As a result, chemical reactions are enhanced at low-temperature. These characteristics are suitable for the removal step in ALE.

In this study, we have investigated the surface state of metal (Ni, Cu) after ALE with GCIB and organic acid using in-situ XPS. Prior to GCIB irradiation, metal surfaces were cleaned by Ar ions. Then Ni or Cu surface were exposed to acetic acids or acetylacetones. The surface layer with adsorbed organic acid on metals were removed by subsequent GCIB irradiation. The difference of the surface states of metal between Ar and O₂-GCIB

irradiation are compared with in-situ XPS results. Etching mechanism by GCIB in the presence of the adsorbed organic acid will be discussed.

9:40am **AP+BI+PS+TF-WeM6 In-situ Characterization of Growth Kinetics of Piezoelectric Films Grown by Atomic Layer Deposition Utilizing an Ultra-high Purity Process Environment**, *Nicholas Strnad*, General Technical Services, LLC; *D.M. Potrepka*, U.S. Army Research Laboratory; *N. O'Toole*, G.B. Rayner, Kurt J. Lesker Company; *J.S. Pulskamp*, U.S. Army Research Laboratory

Recently, $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ (PZT) was grown by atomic layer deposition (ALD) in a piezoelectric film stack that was micro-machined into electrically actuated cantilever beams. [1] ALD PZT is a process technology that may drive 3D PiezoMEMS that utilizes piezoelectric films deposited on micro-machined sidewall structures. AlN is also a desirable piezoelectric for 3D PiezoMEMS but integration has been hampered by its sensitivity to reactive background gases resulting in oxygen contamination of several atomic percent and above. [2] Reactive background gases can also impact oxide films by skewing the non-uniformity and growth-per-cycle (GPC). Thus, individual reactor conditions play a significant role in both the growth kinetics, and resulting quality of thin films grown by ALD. To address both of these issues there exists the need for ultra-high purity (UHP) process capability. Here, we present how the transition from non-UHP to UHP process environment affects ALD AlN and the constituent oxide films in ALD PZT. The UHP process environment also enables the rapid characterization of the reaction kinetics of ALD processes by in-situ ellipsometry. The reaction kinetics of several constituent oxides for ALD PZT are presented based on empirical in-situ observations.

References

[1] Strnad, N.A. (2019) Atomic Layer Deposition of Lead Zirconate-Titanate and Other Lead-Based Perovskites (Doctoral Dissertation) <https://doi.org/10.13016/8dqx-7pev>

[2] Chen, Z. (2019) Thermal atomic layer deposition of aluminum nitride thin films from AlCl_3 (Master's Dissertation)

11:00am **AP+BI+PS+TF-WeM10 Nanoscale Surface Modification of Medical Devices using Accelerated Neutral Atom Beam Technology**, *Dmitry Shashkov*, *J. Khoury*, *B. Phok*, Exogenesis Corp. **INVITED**

Controlling surface properties of biomaterials is vital in improving the biocompatibility of devices by enhancing integration and reducing bacterial attachment. We use Accelerated Neutral Atom Beam (ANAB) technology, a low energy accelerated particle beam gaining acceptance as a tool for nanoscale surface modification of implantable medical devices. ANAB is created by acceleration of neutral argon atoms with very low energies under vacuum which bombard a material surface, modifying it to a shallow depth of 2-3 nm. This is a non-additive technology that results in modifications of surface topography, wettability, and chemistry. These modifications are understood to be important in cell-surface interactions on implantable medical devices. Similarly, ANAB could be used to modify surfaces of medical device coatings (small molecules and proteins), creating a native drug elution barrier. In this study, we characterize the effects of ANAB on several materials including metals (Ti, CoCr) and polymers (PEEK, PP, PVC) and measure the differential ability of eukaryotic versus prokaryotic cell attachment on these modified surfaces. We also study the ability of ANAB to create an elution barrier on a drug coating without the use of binding polymers. We identified that eukaryotic cells including mesenchymal stem cells (MSC) and osteoblasts increase attachment and proliferation on treated surfaces as measured by MTS assay and cell visualization by microscopy. MTS assay shows that by day 14, control PEEK has $9,925 \pm 1,994$ cells while ANAB-treated PEEK has $88,713 \pm 6,118$ cells ($n=3$; $p < 0.0014$). At the same time, we find that bacterial cells including *S.aureus* and *P.aeruginosa* have a decreased ability to bind on the ANAB-treated surface. This dichotomy of cellular attachment may be attributed to the nano-scale surface topography, favoring larger eukaryotic cells while inhibiting attachment of smaller bacterial pathogens. In studies focusing on drug elution, rapamycin was spray-coated on the surface of CoCr bare metal stents and either left as control or ANAB-treated the surface of the drug. These stents were then placed in a plasma elution assay for up to 7 days. We found that untreated stents eluted off most of the drug within 24 hours, and 100% of it by 48 hours post-elution. The ANAB-treated stents, however, showed a favorable elution profile slowly releasing the drug over the 7 day period. ANAB, therefore, has many possible uses in medical device technology in increasing integration, decreasing bacterial attachment and potentially biofilm formation, and, if desired, create an elution profile for a combination drug-device without the use of binding polymers.

11:40am **AP+BI+PS+TF-WeM12 Chemically Enhanced Patterning of Nickel for Next Generation EUV Mask**, *Xia (Gary) Sang*, *E. Chen*, University of California, Los Angeles; *T. Tronic*, *C. Choi*, Intel Corporation; *J.P. Chang*, University of California, Los Angeles

The ever-increasing demand in high-precision pattern definition and high-fidelity pattern transfer in the IC manufacturing industry calls for continuous advancement in lithography technology. Extreme Ultra-Violet (EUV) lithography is being widely adopted for defining sub-10 nm nodes. Due to its ideal optical properties, Ni is under active research as the future absorbing layer material in EUV masks, the profile of which determines the quality of resulting lithographic patterns. Contemporary techniques for patterning Ni rely on noble ion beam milling, which leaves considerable amounts of re-deposition on feature sidewall. Finding chemically selective patterning technique is thus of critical importance. Due to the etch-resistant nature of Nickel, removal at an atomic level is enabled by chemical modification of the surface through plasma exposure and subsequent introduction of organic ligands. Plausible chemicals are first screened by thermodynamic assessments from available databases, experiments were then conducted to validate the theoretical predictions.

Both blanket and patterned Ni thin films were studied using this reaction scheme. Organic chemistries, such as acetic acid and formic acid were first investigated to determine the feasibility of metal-organic formation through direct exposure. The efficacy of acetic acid and formic acid etching chemistries were confirmed through solution-based studies on Ni, the formation of $\text{Ni}(\text{CH}_3\text{COO})_2$ and $\text{Ni}(\text{HCOO})_2$ were confirmed through mass spectrometry. Nickel oxide formation and subsequent removal were confirmed by quantifying the change in the relative intensities of peaks of metallic Ni (852.6 eV) and oxidized Ni (853.7 eV) by X-Ray Photoelectron Spectroscopy (XPS).

The chemical reactivity difference between NiO and Ni²⁺ was quantified in the work to explore the attainable etch selectivity. Due to the decrease in radical concentration and flux, vapor phase etching of metallic Ni resulted in small thickness reduction (~ 0.4 nm/cycle). It is then tested that surface modification, particularly oxidation, is capable of promoting subsequent reactions by lowering reaction energy barrier through metal oxide formation. An oxygen plasma treatment is added prior to acid vapor exposure, and this cyclic approach results in a relatively linear etch rate of ~ 2 nm/cycle, which translates to a 50:1 etching selectivity of NiO over Ni. The same cyclic approach was then applied to patterned samples, post-etch sidewall angle of ~ 85° is measured, which closely conserves the initial feature profile (~ 87°).

12:00pm **AP+BI+PS+TF-WeM13 Surface Reactions of Low Energy Electrons and Ions with Organometallic Precursors and their Relevance to Charged Particle Deposition Processes**, *Rachel Thorman*, Johns Hopkins University; *E. Bilgili*, FAU Erlangen-Nürnberg, Germany; *S. Matsuda*, *L. McElwee-White*, University of Florida; *D. Fairbrother*, Johns Hopkins University

Focused electron beam induced deposition (FE BID) and focused ion beam induced deposition (FIB ID) are nanofabrication techniques where beams of charged particles (electrons or ions) create metal-containing nanostructures by decomposing organometallic precursors in low pressure environments. Consequently, the interactions of electrons and ions with surface-bound organometallic precursors are fundamental processes in these deposition processes. Previously performed ultra-high vacuum (UHV) studies on low energy (below 100 eV) electron interactions with adsorbed precursors (e.g. $\text{Pt}(\text{PF}_3)_4$, MeCpPtMe_3 , and $\text{Co}(\text{CO})_3\text{NO}$) have revealed that electron-induced reactions of surface bound precursors occurs in two sequential steps: (1) an initial step characterized by precursor decomposition/deposition and partial ligand desorption followed by (2) decomposition of the residual ligands. However, a similar level of understanding does not exist for low energy ion interactions with organometallic precursors. In this presentation, I will show that a low temperature, UHV surface science approach can serve as a platform to study the reactions of both low energy electrons (500 eV) and low energy ions (<1kV Ar^+ ions) with organometallic precursors. Results from *in situ* X-ray photoelectron spectroscopy (XPS) and mass spectroscopy (MS) clearly show that low energy electron and ion-induced reactions of several surface-adsorbed species, including $(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_5$, $\text{Ru}(\text{CO})_4$, $\text{Fe}(\text{CO})_5$, and $\text{Co}(\text{CO})_3\text{NO}$, are markedly different. Similarly to electron-induced reactions, low-energy ion-induced reactions proceed in a two-step process with an initial decomposition step primarily characterized by ligand loss. However, ligand loss is typically much more extensive than is observed for electron-induced reactions; for example, in the case of $(\eta^5\text{-Cp})\text{Fe}(\text{CO})_2\text{Re}(\text{CO})_5$ and $\text{Fe}(\text{CO})_5$, all CO ligands desorb in this initial step. The second step in the ion induced reactions can be described as a regime

primarily characterized by physical sputtering. These contrasting results are discussed in the context of different deposition mechanisms proposed for FEBID and FIBID.

Biomaterial Interfaces Division

Room A120-121 - Session BI+AS-WeM

Microbes and Fouling at Surfaces

Moderators: David G. Castner, University of Washington, Kenan Fears, U.S. Naval Research Laboratory

8:00am **BI+AS-WeM1 Hydrophilic Polysaccharides as Building Blocks for Marine Fouling-release Coatings, Axel Rosenhahn, V. Jakobi, X. Cao, W. Yu, T. Gnanasampanthan, R. Wanka, J. Schwarze, J. Koc, Ruhr-University Bochum, Germany; M. Grunze, Heidelberg University, Germany; J.A. Finlay, A.S. Clare, Newcastle University, UK; K.Z. Hunsucker, G.E. Swain, Florida Institute of Technology**

Hydrophilic building blocks like polyethylene glycols are powerful ingredients in modern fouling-release coatings as they are capable to reduce the attractive hydrophobic interactions of microbes with hydrophobic matrix materials such as acrylates, silicones or polyurethanes. We explored how polysaccharides with known antiadhesive and anti-inflammatory properties in medical applications reduce the adhesion of marine fouling organisms. Among the advantages of polysaccharides is their availability, biocompatibility and degradability. Based on previous work on hydrophilic coatings [1] we focused on well hydrated hyaluronans, alginates, chitosans and chondroitin sulfate building blocks. The response of marine organisms and the ability of such components to reduce attachment and facilitate easy removal is explored on grafted monolayers of polysaccharides [2], their amphiphilic derivatives [3], and in more complex coatings such as polysaccharide containing polyelectrolyte multilayers and hybrid polymers. Lab and field experiments will be compared and discussed in the light of the previous notion that uptake of soil particles frequently challenge hydrophilic polymers when used in the real ocean environment [4].

[1] A. Rosenhahn, S. Schilp, J. Kreuzer, M. Grunze, PCCP 2010, 12, 4275

[2] X. Y. Cao, M. E. Pettit, S. L. Conlan, W. Wagner, A. D. Ho, A. S. Clare, J. A. Callow, M. E. Callow, M. Grunze, A. Rosenhahn, Biomacromol. 2009, 10, 907-915.

[3] V. Jakobi, J. Schwarze, J. A. Finlay, K. A. Nolte, S. Spöllmann, H.-W. Becker, A. S. Clare, A. Rosenhahn, Biomacromol. 2018,19, 402-408.

[4] J. Koc, T. Simovich, E. Schönemann, A. Chilkoti, H. Gardner, G.W. Swain, K. Hunsucker, A. Laschewsky, A. Rosenhahn, Biofouling 2019, DOI:10.1080/08927014.2019.1611790

8:20am **BI+AS-WeM2 A Microfluidic Assay to Test the Adhesion of the Marine Bacterium *Cobetia Marina* Under Dynamic Shear Conditions, Jana Schwarze, K.A. Nolte, R. Wanka, V. Jakobi, A. Rosenhahn, Ruhr-University Bochum, Germany**

Microfluidic environments with laminar flow are a useful tool to quantify attachment and removal of marine biofilm formers and cells¹⁻³. We present results on the microfluidic attachment of the marine bacterium *Cobetia marina* (*C. marina*), formerly named *Halomonas marina*, as it is frequently found in marine biofilms^{4,5}. To identify a suitable shear stress for the microfluidic attachment assays, the attachment behavior of *C. marina* was investigated at different shear forces on hydrophobic and hydrophilic surfaces, whereby *C. marina* tends to adhere best on hydrophobic coatings. Among the optimized assay parameters are the relevance of the growth state of *C. marina*. The optimized assay parameters will be presented as well as selected examples how coating chemistries like different self-assembling monolayers, amphiphilic alginates⁶ and different thicknesses of PG coatings⁷ alter the attachment of the marine bacterium *C. marina* under dynamic shear conditions.

1. Christophis, C., Grunze, M. & Rosenhahn, A. Quantification of the adhesion strength of fibroblast cells on ethylene glycol terminated self-assembled monolayers by a microfluidic shear force assay. *Phys. Chem. Chem. Phys.* (2010), 12, 4498-4504. doi:10.1039/b924304f

2. Alles, M. & Rosenhahn, A. Microfluidic detachment assay to probe the adhesion strength of diatoms. *Biofouling* (2015), 31:5, 469-480. doi:10.1080/08927014.2015.1061655

3. Nolte, K. A., Schwarze, J. & Rosenhahn, A. Microfluidic accumulation assay probes attachment of biofilm forming diatom cells. *Biofouling* (2017), 33 (7): 531-543. doi:10.1080/08927014.2017.1328058

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4. Ista, L. K., Fan, H., Baca, O. & López, G. P. Attachment of bacteria to model solid surfaces' oligo(ethylene glycol) surfaces inhibit bacterial attachment. *FEMS Microbiol. Lett.* (1996), 142, 59-63. doi:10.1016/0378-1097(96)00243-1

5. Arpa-Sancet, M. P., Christophis, C. & Rosenhahn, A. Microfluidic assay to quantify the adhesion of marine bacteria. *Biointerphases* (2012), 7, 26. doi:10.1007/s13758-012-0026-x

6. Jakobi, V. et al. Amphiphilic Alginates for Marine Antifouling Applications. *Biomacromolecules* (2018), 19, 402-408. doi:10.1021/acs.biomac.7b01498

7. Wanka, R. et al. Fouling-Release Properties of Dendritic Polyglycerols against Marine Diatoms. *ACS Appl. Mater. Interfaces* (2018), 10, 34965-34973. doi:10.1021/acsami.8b12017

8:40am **BI+AS-WeM3 Biofilm Mechanics as a Mechanism for Survival on Surfaces from Medical Device to Ship Hulls, Paul Stoodley, Ohio State University**

INVITED

Bacterial biofilms are microscopic assemblages of bacterial cells usually attached to a surface and held together by a self-produced extracellular polymeric slime (EPS) matrix. Biofilms are ubiquitous in the natural environment and are highly problematic in industry and medicine where they cause corrosion, fouling, contamination and chronic medical and dental infections. The basic biology of bacterial biofilm development and strategies evolved to survive in the environment of the ancient earth are now used by the bacteria to survive on modern man-made materials. Diffusion limitation within the EPS matrix results in sharp gradients as nutrients are consumed by respiring bacteria on the periphery faster than they can diffuse in. Similarly, cell signals (molecules used to co-ordinate behavior between individual cells) and waste products, such as fermentation acids, build up in the interior of the biofilm. Biofilms are mechanically complex showing a range of behaviors from elastic solids to viscous liquids. These viscoelastic properties can facilitate survival on surfaces exposed to high shear stresses and can explain the high pressure drop and frictional losses in pipelines and ship hull fouling. However, the mechanical response may also be exploited to drive antimicrobials into the biofilm for control. The development of microenvironments combined with the structural versatility of the biofilm is the basis for the distinct biofilm phenotype as an emergent property of population of single cells and is a challenge to overcome in their control.

9:20am **BI+AS-WeM5 Dendritic Polyglycerols as Fouling-release Coatings Against Marine Hard- and Soft Foulers, Robin Wanka, Ruhr-University Bochum, Germany; N. Aldred, J.A. Finlay, Newcastle University, UK; K.A. Nolte, J. Koc, Ruhr-University Bochum, Germany; H. Gardner, K.Z. Hunsucker, G.E. Swain, Florida Institute of Technology; C. Anderson, A.S. Clare, Newcastle University, UK; A. Rosenhahn, Ruhr-University Bochum, Germany**

Polyethylene glycol (PEG) containing coatings show outstanding antifouling properties, which is commonly assigned to their hydrophilicity and their highly hydrated nature. A structurally related but hyperbranched version are polyglycerols (PGs) that increase the spatial density of non-fouling polymer units and decrease the defect density in coatings.^{1,2} So far they were successfully applied in biomedicine against attachment by pathogenic bacteria. Using a surface initiated ring opening polymerization reaction³, we grafted dendritic PGs on surfaces. The resulting samples were characterized by spectroscopic ellipsometry, contact angle goniometry, ATR-FTIR, and by degradation experiments. The prepared surfaces show excellent protein-resistance. The fouling release properties were tested in a standardized lab assay with diatoms (*Navicula incerta*) and in a dynamic field assay⁴ at the FIT test site in Florida. The initial attachment of diatoms under static conditions was similar on the PGs as compared to a hydrophobic control. However, PGs show outstanding fouling release properties. Up to 94% of attached diatoms could be removed from the coatings after the exposure to a shear stress of 19 Pa. These results were confirmed in the field assays.⁵ The range of testes species was also extended to macro-fouling organisms such as zoospores of green algae (*Ulva linza*) and barnacle larvae (*Balanus amphitrite*).

(1) Wyszogrodzka, M.; Haag, R. Synthesis and characterization of glycerol dendrons, self-assembled monolayers on gold: A detailed study of their protein resistance. *Biomacromolecules* 2009, 10, 1043-1054.

(2) Siegers, C.; Biesalski, M.; Haag, R. Self-assembled monolayers of dendritic polyglycerol derivatives on gold that resist the adsorption of proteins. *Chemistry* 2004, 10, 2831-2838.

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(3) Weber, T.; Gies, Y.; Terfort, A. Bacteria-Repulsive Polyglycerol Surfaces by Grafting Polymerization onto Aminopropylated Surfaces. *Langmuir* **2012**, *28*, 15916–15921.

(4) Nolte, K. A.; Koc, J.; Barros, J. M.; Hunsucker, K.; Schultz, M. P.; Swain, G. E.; Rosenhahn, A. Dynamic field testing of coating chemistry candidates by a rotating disk system. *Biofouling* **2018**, *49*, 1–12.

(5) Wanka, R.; Finlay, J. A.; Nolte, K. A.; Koc, J.; Jakobi, V.; Anderson, C.; Clare, A. S.; Gardner, H.; Hunsucker, K.; Swain, G. W. *et al.* Fouling-Release Properties of Dendritic Polyglycerols against Marine Diatoms. *ACS applied materials & interfaces* **2018**, DOI: 10.1021/acsami.8b 12017 .

9:40am **BI+AS-WeM6 Nano- and Microscale ZnO with Controllable Abundance of Surface Polarity as a Platform to Study Antibacterial Action.**, J.M. Reeks, B. Thach, Texas Christian University; W. Moss, Texas State University; R. Maheshwari, Texas Academy of Mathematics and Science; I. Ali, S.M. McGillivray, Yuri Strzhemechny, Texas Christian University

Nano- and microcrystalline ZnO is a low-cost, easy to synthesize material employed in many current and incipient applications owing to its exceptional optoelectronic, structural and chemical characteristics as well as a broad range of production techniques. Antibacterial action of ZnO is one of these applications, with a growing field of interdisciplinary research. Despite numerous and vigorous studies of the antibacterial nature of ZnO, and, in particular, the well- documented antimicrobial action of micro- and nanoscale ZnO particles, the most fundamental physical and chemical mechanisms driving this action are still not well identified. In particular, the influence of the crystal surface polarity on the antibacterial performance is largely unknown. Normally, hexagonal (wurtzite) ZnO crystals can be terminated with either charged polar (Zn or O) or electrically neutral nonpolar surfaces. In this work, we employ a hydrothermal growth protocol to produce ZnO nano- and microcrystals with tunable morphology, in particular to obtain a dependable control of the prevalent polarity of the free surfaces. This, in turn, can serve as a platform to investigate antibacterial action mechanisms in the synthesized specimens. It is reasonable to assume that one of the key phenomena behind such action is rooted in interactions between ZnO surfaces and the extracellular layers. Thus, excess charge or lack thereof, surface electronic charge traps, as well as variations in the stoichiometry at surfaces with different polarities of ZnO particles may affect interfacial phenomena with cell surfaces. It is possible therefore that the relative abundance of ZnO surfaces with different polarities could significantly influence their antibacterial action. In our studies, we produced ZnO crystals comparable in size with the bacteria employed in our assays, such as *S. aureus*. This was done intentionally in order to avoid cellular internalization of ZnO particles and thereby to address primarily the mechanisms involving ZnO/cell surface interface. These experiments were performed in conjunction with optoelectronic studies of ZnO crystals (photoluminescence, surface photovoltage) to characterize electronic structure and dominant charge transport mechanisms as fundamental phenomena governing antibacterial characteristics of our samples. We report on the results of these comparative studies relating predominant ZnO surface polarity with the antimicrobial action.

11:00am **BI+AS-WeM10 Patterning Bacteria at Interfaces with Bio-Inspired Vascularized Polymers**, K. Marquis, B. Chasse, Caitlin Howell, University of Maine

Nearly all methods of introducing bioactive compounds to the surface of a substrate rely on application from above or fail over time due to depletion. In this work, we use a bio-inspired approach to deliver target molecules to an interface from below, making use of both theoretical modeling and experimental validation to rationally design customizable patterns and gradients. Mimicking the vascular systems of living organisms, networks of empty 3D-printed channels are filled with liquid containing the compound of interest, which flows through the vascular network and diffuses through the polymer, eventually reaching the substrate surface. In proof-of-principle experiments using *Escherichia coli* and *Staphylococcus epidermidis* as model organisms, we demonstrate both theoretically and experimentally that the concentration of antibiotic and duration over which it is delivered to the surface can be controlled by varying the location of the vascular channels and concentration of the antibiotic solution inside. The result is a well-defined and predictable patterned response from the bacteria growing on the surface, a first step toward developing new types of adaptive antifouling surfaces and cell culture tools.

11:20am **BI+AS-WeM11 Chemical Imaging of Root-Microbe Interactions**, Vaithiyalingam Shutthanandan, A. Martinez, R. Boiteau, Pacific Northwest National Laboratory

Nutrient mobilization from soil minerals is critical for plant growth, particularly in marginal lands with high pH soils or low phosphate and iron availability. Rhizospheric bacteria enhance plant growth by converting root exudates such as sugars and amino acids into organic acids and chelating molecules that enhance mineral dissolution and improve the availability of nutrients such as phosphorous and iron. Hence, understanding the effect of iron availability on metabolite exchange between plant and micro-organism is crucial. The spatial proximity of bacteria to root tissue of specific composition and sites of root secretion is one key aspect of this exchange. In this work, the model grass *Brachypodium* and the bacteria *Pseudomonas fluorescens* are used as a model system for studying rhizosphere interactions that improve metal bioavailability. *Brachypodium* was grown under four different conditions such as: (1) + Fe, (2) – Fe, (3) + *Pseudomonas* + Fe, (4) + *Pseudomonas* – Fe. The plants were grown for 2 weeks in the hydroponic solution and removed from the system and the root samples were analyzed using Helium Ion Microscope (HIM) for spatial organization of bacteria within the rhizosphere of *Brachypodium* and X-ray photoelectron spectroscopy (XPS) for chemical imaging. HIM results clearly show bacteria colonies on the root surfaces. However, these colonies were populated preferentially within grooved structures along the surface of the root. We hypothesize that there are compositional differences in the surface of the root area that explain the presence of these 'hotspots'. Roots exposed with iron show larger bacteria colonies than the roots without iron content. XPS imaging measurements on these samples revealed four predominant compositional classes, lipids/lignin, protein, cellulose and uronic acid that were spatially resolved across the surface of the main root with ~10 nm resolution. Carbon and oxygen concentrations were almost constant among these samples and also constant along the individual roots. On the other hand, there is a clear variation in the concentrations of nitrogen and potassium along the root as well as among the samples. Discussion on the results and their implications will be discussed in this presentation.

11:40am **BI+AS-WeM12 Biocompatible Silver Nanoparticles-loaded Chitosan Membranes with Antibacterial Activity Produced by Directed Liquid-Plasma Nanosynthesis**, Camilo Jaramillo, A.F. Civantos, A. Mesa, J.P. Allain, University of Illinois at Urbana-Champaign

Silver nanoparticles (Ag NPs) possess remarkable antibacterial properties that are widely recognized. The emergence of antibiotic-resistant bacteria has motivated the interest of Ag NPs as an alternative for antimicrobial protection, in a wide range of applications [1]. However, Ag NPs have also shown toxicity and low biocompatibility. In addition, their synthesis usually involves toxic compounds, further limiting their applicability as a biomaterial. Research on Ag NPs has largely focused on increasing their biocompatibility. Properties such as NPs size, dispersity, and stability have shown to play an important role on their biocompatibility [2]. Green synthesis methods that require non-toxic agents while giving control over these properties are of high interest.

Chitosan (CS) is a deacetylated derivative of chitin, a widely available polymer. Its properties include biodegradability, biocompatibility and non-toxicity, making it an attractive alternative for biomaterials. CS has been used as a bioactive coating (for proteins, drugs and antibiotics) and as a stabilizing agent in the production of Ag NPs [3]. Approaches to synthesize CS-based Ag NPs include γ irradiation and sonochemical methods [4].

In this work, Directed Liquid-Plasma Nanosynthesis (DLPNS) was used to drive Ag NPs synthesis without the need of other reagents. CS membranes were used to immobilize the NPs, to explore their application as an antibacterial coating for biomaterials. The Ag NPs precursor concentration and irradiation time were used as control parameters. Surface topography and chemistry were studied by SEM, Contact Angle, XRD and EDS. Antimicrobial properties of the membranes were evaluated against gram-positive (*S. aureus*) and gram-negative (*E. coli*) bacteria. Life and death assays revealed the antibacterial activity of the membranes. To study their biocompatibility and cytotoxicity, mammalian cell cultures were used. Cell viability, adhesion and metabolism were evaluated via Alamar blue and immunostaining tests. SEM images were used to assess the presence of Ag NPs in the CS matrix, and observe the bacteria and cell morphology on the surface of the membranes.

[1] D. Wei, W. Sun, W. Qian, Y. Ye, X. Ma, Carbohydr. Res. 344 (2009) 2375–2382.

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[2] E.I. Alarcon, M. Griffith, K.I. Udekwu, eds., Silver Nanoparticle Applications, Springer International Publishing, Cham, 2015.

[3] A. Civantos, E. Martínez-Campos, V. Ramos, C. Elvira, A. Gallardo, A. Abarrategi, ACS Biomater. Sci. Eng. 3 (2017) 1245–1261.

[4] N.M. Huang, S. Radiman, H.N. Lim, P.S. Khiew, W.S. Chiu, K.H. Lee, A. Syahida, R. Hashim, C.H. Chia, Chem. Eng. J. 155 (2009) 499–507.

12:00pm **BI+AS-WeM13 Multifunctional 2D MoS₂-Based Nanoplatfom for Multimodal Synergistic Inactivation of Superbugs, Paresh Ray**, Jackson State University

Development of new antibacterial therapeutic materials is becoming increasingly urgent due to the huge threat of superbugs, which are responsible for more than half of a million deaths each year in this world. We will discuss our recent report on the development of a novel nanobiomaterial based on a melittin antimicrobial peptide (AMP)-attached transition metal dichalcogenide MoS₂-based theranostic nanoplatfom. The reported nanoplatfom has a capability for targeted identification and synergistic inactivation of 100% multidrug-resistant superbugs by a combined photo thermal therapy (PTT), photodynamic therapy (PDT), and AMP process. A novel approach for the design of a melittin antimicrobial peptide-attached MoS₂-based nanoplatfom is reported, which emits a very bright and photo stable fluorescence. It also generates heat as well as reactive oxygen species (ROS) in the presence of 670 nm near-infrared light, which allows it to be used as a PTT and PDT agent. Due to the presence of AMP, multifunctional AMP exhibits a significantly improved antibacterial activity for superbugs via a multimodal synergistic killing mechanism. Reported data demonstrate that nanoplatfoms are capable of identification of multidrug-resistant superbugs via luminescence imaging. Experimental results show that it is possible to kill only ~45% of superbugs via a MoS₂ nanoplatfom based on PTT and PDT processes together. On the other hand, killing less than 10% of superbugs is possible using melittin antimicrobial peptide alone, whereas 100% of methicillin-resistant *Staphylococcus aureus* (MRSA), drug-resistant *Escherichia coli* (*E. coli*), and drug-resistant *Klebsiella pneumoniae* (KPN) superbugs can be killed using antimicrobial peptide-attached MoS₂ QDs, via a synergistic killing mechanism.

New Challenges to Reproducible Data and Analysis Focus Topic

Room A124-125 - Session RA+AS+BI-WeA

Addressing Reproducibility Challenges using Multi-Technique Approaches

Moderators: Tony Ohlhausen, Sandia National Laboratory, Vincent Smentkowski, GE-Research

2:20pm **RA+AS+BI-WeA1 Responding to New and Old Challenges to Data, Analysis and Scientific Study Reproducibility, Donald Baer**, Pacific Northwest National Laboratory; *I.S. Gilmore*, National Physical Laboratory, UK

An increasing number of studies, surveys and editorials highlight experimental and computational reproducibility and replication issues that frequently appear in most areas of modern science. In a 2018 AVS conducted survey, 66% of those responding identified reproducibility as a significant issue. There are multiple and complex causes of what some have called a "reproducibility crisis," which can impact materials, interface/(bio)interphase, vacuum and others sciences of importance to AVS members. Reproducibility challenges are not new, but now appear in both old and new forms requiring innovative solutions. Drivers influencing reproducibility problems include the increasingly multi-discipline, multi-method nature of much advanced science, increased complexity of the problems and systems being addressed, and the large amounts and multiple types of experimental and computational data being collected and analyzed in many studies. Such issues challenge experimental teams and the review process. Systematic and sustained efforts are needed to address the causes of reproducibility problems that can hinder the rate of scientific progress and lower public and political regard for science. The Focus topic New Challenges to Reproducible Data and Analysis aims to raise awareness of the challenges, examine the causes, impacts of reproducibility problems and explore approaches that can help address both the newer and older generation of reproducibility challenges. Some problems and solutions are easy to identify, even if not readily implemented. Other drivers and causes are less obvious and therefore harder to address. This talk will introduce the focus topic sessions, review key literature on the topic of reproducibility and summarize how the presentations fit together as a way to address reproducibility challenges.

2:40pm **RA+AS+BI-WeA2 Achieving Reproducible Data: Examples from Surface Analysis in Semiconductor Technology, Thierry Conard, P.A.W. van der Heide, A. Vanleenhove, C. Zborowski, W. Vandervorst**, IMEC, Belgium

Repeatability and reproducibility in surface analysis in the semiconductor industry are key to for supporting efficient process development as well as High Volume Manufacturing (HVM). As two examples, long term repeatability is critically important when comparing to historical data, while reproducibility is required to support technology transfers when HVM of specific devices is to be carried out at multiple sites. This however introduced a number of unique challenges for running a characterization facility.

In this presentation we will present a number of examples that can result in reproducibility issues. Particular focus will be in the areas of X-ray Photoelectron Spectroscopy (XPS) Secondary Ion Mass Spectrometry (SIMS). The first and foremost causes of repeatability and reproducibility arise from instrumental variation. A second important source arises from samples variability. We will show that assessing long-term instrumental stability is potentially hindered by long term variation of samples characteristics. We will also show that an understanding of the characterization techniques is paramount to understanding such issues.

Next to the "pure" technical causes of repeatability and reproducibility, is the human factor. This involve for instance decision making in data treatment during for example, fitting procedures, statistical treatments, etc. This will be illustrated using practical examples. And with present day characterization depending more heavily on computational support/commercial software, potential detriments to characterization repeatability will again be made evident. Finally, we will show through round-robin results, that combining all the above factors, widely varying results can be obtained on the same samples.

3:00pm **RA+AS+BI-WeA3 New Challenges in Analytical Reproducibility Illustrated with Old and New Case Studies, Thomas Beebe Jr**, University of Delaware

INVITED

To address the subject of this session's topic, "New Challenges to Reproducible Data and Analysis," I have chosen to select a few case studies from my research group's work over the past 30 years. My examples will therefore be drawn from the methods and techniques that I have employed: XPS, TOF-SIMS, AFM, STM, and from the surface-related fields in which we have worked: biomolecules on surfaces, molecular self-assembly, biomaterials, and perhaps some others. It has always been my goal and approach to employ careful controls, scientific statistics, and data extraction to the richest extent possible.

4:20pm **RA+AS+BI-WeA7 Challenges and Approaches to Addressing Reproducibility in Biointerface Science and Engineering, Sally McArthur**, Swinburne University of Technology and CSIRO, Australia, Australia

INVITED

Our publications should serve as guides to repeat our experiments/analyses and reproduce the results; however, quite often we may find ourselves not able to do so. Over the past few years, there have been many papers and editorials that have shown that issues associated with Repeatability, Reproducibility, and Replicability impact almost all areas of science, and in an AVS-conducted survey, 65% of those responding indicated that they have seen or experienced significant reproducibility issues when they have sought to recreate experiments from the literature. It is clear that the increasing demands of complex research requiring use of multiple experimental and computational research methods is a central theme. The challenge in the Biointerface Science community is compounded by the inherent variability of biology. Working at the interface between the physical and life sciences, it is often difficult for us to have in-depth knowledge of the idiosyncrasies of the many techniques we use and we need to be aware of for our data interpretation. This talk will discuss approaches we are taking to tackle this issue within the Biointerface Science Community and the journal Biointerphases. We will look at how we can champion best practices, sharing our knowledge across our community, and seek to support researchers who are new to the field or want to explore new techniques to avoid the pitfalls and better understand both the opportunities and limitations of the techniques, methods, and approaches used in our multidisciplinary community.

Sally L McArthur, Editor Biointerphases

5:00pm **RA+AS+BI-WeA9 Complementary Measurements of Colloidal Nanoparticles and their Coatings by In-situ and Vacuum-based Methods, Caterina Minelli**, National Physical Laboratory, UK

INVITED

Engineered nanoparticles add high value to commercial products and have the potential to improve our quality of lives and boost prosperity. For example, they provide radical new approaches to cancer drug delivery, biosensing, medical imaging and catalysis. However, the effective implementation of these materials relies on the ability to measure and control their properties, such as their surface chemical identity, size and concentration. There are significant challenges in the analysis of nanomaterials due to, among other factors, the interdisciplinary nature of the field and the lack of adequate reference materials to calibrate analytical tools. The use of complementary tools provides opportunities for (1) deepening the quantitative understanding of these systems and, importantly, (2) a route to method validation. I will provide examples from our work on both these cases.

(1) We use a combination of methods to analyse nanoparticles which are employed in liquid media (*in-situ*) using techniques such as analytical centrifugation and dynamic light scattering and *ex-situ* with X-ray photoelectron spectroscopy (XPS). Sound sample preparation protocols are critical for meaningful and comparable measurements. This is especially important when using complementary methods for the analysis of the same samples. I will discuss our experience in the analysis of protein coated gold nanoparticles and polymeric core/shell nanoparticles and show how multimodal analysis is critical to the full understanding of the system.

(2) The lack of certified reference materials for nanoparticle number concentration has hindered the validation of laboratory methods, which resulted in a general distrust in commercially available instrumentation. We have led a collaborative effort to develop accurate methods based on small angle X-ray scattering (SAXS) and single particle inductively coupled plasma mass spectrometry (spICPMS) for the measurement of colloidal number concentration. We have then used these methods to assess and validate a range of laboratory methods. I will discuss the result of this work for both ideal and agglomerated nanoparticles and present the outcomes

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of a large VAMAS interlaboratory study which assessed four methods for the measurement of colloidal concentration.

Finally, I will look at unmet challenges in the characterisation of nanoparticles and discuss the benefits of a multimodal approach to them.

5:40pm RA+AS+BI-WeA11 Multiple Technique Analysis of Perovskite Materials used in Battery and Fuel Cell Components, Robin Simpson, P. Mack, T.S. Nunnery, Thermo Fisher Scientific, UK

Due to the worlds ever increasing energy needs, renewable sources, higher efficiency and energy storage have become important research areas. Therefore, full analysis of the materials used in such applications can add to our understanding of these emerging technologies. In many cases this will mean using several techniques on a single sample.

The chemical composition of the materials found in batteries or fuel cells play a huge part in the desired properties. An example of this is in the inclusion of Sr^{2+} in the A sites of lanthanum manganite. This increases the electronic conductivity of cathode material via the addition of electronic holes to the perovskite structure. XPS allows us to quantify the chemistry of the material and use that data to further improve its properties.

Chemical analysis of the surface of the material by XPS also allows us to identify diffusion or segregation effects that can occur once a battery material has been cycled. Once a build-up of surface material on an electrode becomes too thick ions cannot pass between them, preventing charging of a cell. Using XPS with other techniques like ISS allows us to characterise the surface material (\sim top 10 nm) and the surface monolayer.

Here we discuss a LaSrFeCoO perovskite sample typically found in fuel cell and battery cell electrode materials. XPS is used to quantify the composition of the material and identify the La chemical bonding state to find the sample contains La_2O_3 bonding. ISS is also utilised to show no significant Fe and Co at the top surface of the sample. Comparing this to the XPS data taken from the top 10 nm of the shows signs of Fe and Co depletion at the surface.

The perovskite materials are also found in solar cell components. These materials are often used due to their high efficiencies but also because the material band gap is tuneable therefore allowing us to optimise the material composition. Using a technique like REELS combined with XPS can enable us to measure the band gap of the material to reveal the efficiency as well as identify the composition. In this case the band gap of the sample was calculated at 6.3 eV using REELS.

We will also be discussing the use of coincident XPS/Raman to investigate the bulk and surface characteristics of the LaSrFeCoO sample without exposing it to atmosphere between analysis.

6:00pm RA+AS+BI-WeA12 Mapping Local Physical Properties by Combining ToF-SIMS Analysis with Advanced Scanning Probe Microscopy, Maiglid Andreina Moreno Villavicencio, N. Chevalier, J.-P. Barnes, CEA-LETI, France; P. Kermagoret, F. Lorut, ST Microelectronics, France; B. Gautier, Université de Lyon, France

The continuous miniaturization and complexity of micro-devices have pushed existing characterization techniques to their limits. The correlation of techniques has emerged to overcome this issue and provide precise and accurate characterization. We have focused our research on combining and studying the applications of two specific techniques: time-of-flight secondary ion mass spectrometry (ToF-SIMS) and atomic force microscopy (AFM). The ToF-SIMS is a high-performance technique to chemically analyze a sample in 3-dimensions with a lateral resolution of 100 nm. On the other hand, the AFM is a high-resolution technique to obtain maps of the topography and local physical properties with a lateral resolution of 10 nm.

A ToF-SIMS / AFM methodology that combine the topographical information with the chemical composition has been established [1]. It was used to achieve a topography-corrected 3D ToF-SIMS data set and maps of local sputter rate where the effect of roughness and vertical interfaces are seen. However, the correlation of these characterization techniques is not limited to these applications. Indeed, by using advanced operation modes of the AFM, maps of diverse physical properties of the sample can be obtained at the same time as the topography.

We have explored the combination of ToF-SIMS analysis with three AFM advanced modes: piezoresponse force microscopy (PFM), scanning capacitance microscopy (SCM) and scanning spreading resistance microscopy (SSRM). These operation modes respectively allow to map ferroelectric domains, to locally measure capacitance variations and to image the sample surface resistivity.

The combined ToF-SIMS / AFM methodology was applied ex-situ per individual AFM mode on diverse samples for applications focused on micro-electronics. We will present here some promising results highlighting the strength and the perspectives of the expansion of this combination to other applications.

[1] M.A. Moreno et al, J. Vac. Sci. Technol. B 36 (2018) 03F122.

Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+2D+AS+BI+NS-ThM

Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces II

Moderators: Utkur Mirsaidov, National University of Singapore, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am CA+2D+AS+BI+NS-ThM1 From Surfaces to Solid-Gas and Solid-liquid Interfaces: Ambient Pressure XPS and Beyond, *Miquel B. Salmeron*, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The rapidly increasing field of surfaces under ambient conditions of temperature and pressure, in gas and liquid environments, reflects the importance of understanding surface properties in conditions closer to practical situations. A lot of progress has been made in the last two decades, enabled by the emergence of a number of new techniques, both spectroscopy and microscopy, that can deliver atomic scale information with the required surface/interface sensitivity. I will present recent advances with examples that illustrate the novel understanding derived from the use of new techniques. One in the gas–solid interface where two important barriers have been bridged: the pressure gap, and the temperature gap. These gaps are very important when dealing with weakly bound molecules, where only in the presence of gas at a suitable pressure, or at low temperatures, a non-negligible coverage of adsorbed molecules can be achieved. The temperature gap manifests also in the removal of kinetic barriers. By bridging these two gaps a host of new interface structures have been unveiled that bring new understanding to catalytic phenomena. This will be illustrated with the examples of Cu and CuCo alloys in the presence of CO. In the case of solid-liquid interfaces, the introduction of new methods using well established x-ray spectroscopies is opening the way to the study of the important electrical double layer structure as a function of applied bias, as I will illustrate with the application of X-Ray absorption and IR to sulfuric acid-Pt and Ammonium Sulfate-graphene interfaces.

8:40am CA+2D+AS+BI+NS-ThM3 Probing Solid-liquid Interfaces with Tender X-rays, *Zbynek Novotny, N. Comini, B. Tobler*, University of Zuerich, Switzerland; *D. Aegerter, E. Fabbri*, Paul Scherrer Institute, Switzerland; *U. Maier*, Ferrovac GmbH, Switzerland; *L. Artiglia, J. Raabe, T. Huthwelker*, Paul Scherrer Institute, Switzerland; *J. Osterwalder*, University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in the condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy ranging between 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source that combines ambient-pressure XPS with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [1], and by using tender X-rays (2-8 keV) from the Phoenix beamline, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces (see Supplementary document). Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film. This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and outline the future directions we are going to pursue using this new instrument.

[1] S. Axnanda, E. J. Crumlin et al., *Sci. Rep.* 5, 09788 (2014).

9:00am CA+2D+AS+BI+NS-ThM4 X-ray Photoelectron Spectroscopy Insight into X-ray Induced Radiolysis at Heterogeneous Liquid Electrolyte Interface, *Christopher Arble*, National Institute of Standards and Technology (NIST); *H. Guo*, Southeast University, China; *E. Strelcov, B. Hoskins*, National Institute of Standards and Technology (NIST); *M. Amati, P. Zeller, L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy; *A. Kolmakov*, National Institute of Standards and Technology (NIST)

Assessing chemical processes of electrolyte interfaces under operando conditions is an aspirational goal of great importance to many industrial applications¹ that remains technically challenging to investigate. XPS is a powerful characterization tool that can probe elemental and chemical information of atoms with nanoscale depth sensitivity but has traditionally been restricted to UHV conditions. There has been a concerted effort to enable quantitative in-situ measurements of gas and liquid interfaces under realistic environments.²⁻⁴ Recently, advances in 2D materials, i.e., graphene, have been utilized to probe heterogeneous interfaces through molecularly impermeable, electron transparent membranes to maintain UHV pressure in the analysis chamber.⁵

Herein we apply photoemission spectromicroscopy to study the electrochemical dynamics of an array of several thousand individual electrolyte cells encapsulated with electron transparent bilayer graphene.⁶ We monitored the chemical speciation at the electrode- aqueous CuSO₄ electrolyte interface as a function of potential. During the electrochemical experiments, the effects of irradiation upon the solution were observed to influence the system, and spectral deconvolution identified oxidized species of copper and oxygen as well as reduced states of sulfur that were connected to reaction pathways tied with radiolysis. Corresponding SEM images and subsequent EDS spectral maps display spatially confined irradiated byproducts which can be associated with the species observed in with XPS.

Observations of XPS spectroscopic regions in the system were taken at varied X-ray dosages to probe the impacts of radiolysis on the liquid solution concerning the spectroscopic observation of electrochemical deposition of Cu. This experimental methodology imparts a greater understanding of the influence of X-ray induced water radiolysis processes towards the quantification of the electrode/electrolyte interfaces and the underlying dosages necessary for artifact-free data acquisition in condensed media.

References:

1. Saveant, J., *Chemical Reviews* **2008**, 108, (7), 2348-2378
2. Siegbahn, H., *J. Phys. Chem.* **1985**, 89, (6), 897-909
3. Salmeron, M.; Schlögl, R., *Surf. Sci. Rep.* **2008**, 63, (4), 169-199
4. Starr, D.; et al., *Chem. Soc. Rev.* **2013**, 42, (13), 5833-5857
5. Kraus, J.; et al., *Nanoscale* **2014** 6, (23), 14394-14403
6. Yulaev, A.; et al., *ACS Appl. Mater. Interfaces* **2017**, 9, (31) 26492-26502

9:20am CA+2D+AS+BI+NS-ThM5 Theoretical Investigation of Reactivity at Complex Solid-Liquid Interfaces, *R. Rousseau, Manh Nguyen*, Pacific Northwest National Laboratory **INVITED**

Contrary to solid/gas interfaces, in solid/liquid interfaces the molecules in the liquid can be organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydrophilicity of the support. In this talk, we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab initio molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces, and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in

the double layer as well as its orientation with respect to the electrode surface. While both examples included have been drawn from the upgrading of bio-oil ex pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.

References

1. Cantu DC, Wang YG, Yoon Y, Glezakou VA, Rousseau R, Weber RS. 2016, *Catalysis Today*, <http://dx.doi.org/10.1016/j.cattod.2016.08.025>
2. Perez Y, Fajardo M, Corma A. 2011, *Catalysis Communications*, 12, 1071-1074.
3. Padmaperuma AB, Cantu DC, Yoon Y, Nguyen MT, Wang YG, Glezakou VA, Rousseau R, Liga MA. Manuscript in preparation, to be submitted.

11:00am **CA+2D+AS+BI+NS-ThM10 In-situ/Operando Soft X-ray Spectroscopy for Interfacial Characterization of Energy Materials and Devices**, Y.-S. Liu, X. Feng, *Jinghua Guo*, Lawrence Berkeley National Laboratory

In-situ/operando soft x-ray spectroscopy offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment of elements and other critical information of solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando capabilities for the characterization of interfacial phenomena in energy materials and devices.

A number of the experimental studies, which revealed the catalytic and electrochemical reactions in real time, will be presented, e.g. solid (metal film)/liquid (water) electrochemical interface, Mg-ion batteries, and Li-S batteries [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectroscopy characterization provides the unique information for understanding the real reaction mechanism.

References:

1. "Mg deposition observed by in situ electrochemical Mg K-edge X-ray absorption spectroscopy", T. S. Arthur, P.-A. Glans, M. Matsui, R. Zhang, B. Ma, J.-H. Guo, *Electrochem. Commun.* **24**, 43 (2012)
2. "The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy", J. J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J.-H. Guo, D. Prendergast and M. Salmeron, *Science* **346**, 831 (2014)
3. "Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery", M. Ling, L. Zhang, T. Zheng, J. Feng, J.-H. Guo, L. Mai, G. Liu, *Nano Energy* **38**, 82 (2017).
4. "Interfacial insights from operando sXAS/TEM for magnesium metal deposition with borohydride electrolytes", T. Arthur, P.-A. Glans, N. Singh, O. Tutusaus, K. Nie, Y.-S. Liu, F. Mizuno, J.-H. Guo, D. H. Alesm, N. Salmon, R. Mohtadi, *Chem. Mater.* **29**, 7183 (2017).

"Revealing the Electrochemical Charging Mechanism of Nanosized Li₂S by in Situ and Operando X-ray Absorption Spectroscopy", L. Zhang, D. Sun, J. Feng, E. Cairns, J.-H. Guo, *Nano Lett.* **17**, 5084 (2017).

11:20am **CA+2D+AS+BI+NS-ThM11 The Importance of Amino Acid Adsorption on Polymer Surfaces in *P. Aeruginosa* Biofilm Formation**, *Olutoba Sanni*, University of Nottingham, UK

High throughput materials discovery screens have revealed polymers that reduce bacterial surface colonization which have progressed to currently ongoing clinical trials [Hook *et al.* *Nature Biotech* 2012]. These novel poly (meth)acrylate coatings reduced biofilm formation by *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli* in laboratory cultures *in vitro* and *in vivo* in a mouse foreign body infection model. These coatings are known to function by preventing biofilm formation, however why the bacterial cells respond in this way to these polymers has yet to be elucidated. The initial interaction between bacteria and surfaces has been identified as a key determining factor when bacteria decide to either irreversibly attach and colonise a surface or not.

The exposure of most materials to biological milieu is accompanied by adsorption of biomolecules. In protein containing media there is a strong relationship between the adsorbed protein layer formed on materials and

mammalian cell attachment. However, in protein-free media such as used by Hook *et al.*, this cannot be a contributor to early bacterial cell attachment. Consequently, here we carry out careful surface chemical analysis on two polymers known to exhibit drastically different biofilm formation in a standard protein-free, amino acid containing bacterial culture medium (RPMI).

Time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analysis determined that high amino acid adsorption correlates with the surface exhibiting low *P. aeruginosa* colonisation. A total of 10 peaks characteristic of specific amino acids were identified by ToF-SIMS to be adsorbed on polymer. We successfully fitted the Freundlich and Langmuir adsorption isotherm models from which we determined adsorption capacity of polymers, calculated the on/off rate of amino acid adsorption on both anti-biofilm and pro-biofilm surfaces. With XPS, the overlayer coverage of amino acids on the polymer surface was established to be approximately 0.2 nm.

The study was extended to quantify in high throughput manner the adsorption of amino acids from RPMI media onto surfaces of 288 polymer materials printed onto a microarray. Ion fragments generated from ToF-SIMS were used to produce a regression model from which we identified polymers with cyclic moieties as major promoters of amino acid adsorption.

This is the first report suggesting adsorbed amino acids or other adsorbed nutrients may correlate with the biofilm formation tendency of materials.

Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM+BI+SS-ThM

Material Stabilities and Technology for Degradation Protection

Moderators: Markus Valtiner, Vienna University of Technology, Austria, Gareth S. Parkinson, TU Wien, Austria

8:00am **DM+BI+SS-ThM1 Extremely Thin Protective Oxide Layer for Reflective Silver Thin Films**, *Midori Kawamura, E. Kudo, Y. Sasaki, T. Kiba, Y. Abe, K.H. Kim*, Kitami Institute of Technology, Japan; *H. Murotani*, Tokai University, Japan

Silver (Ag) thin films possess high electrical and optical properties, but their low stability should be resolved. We have developed a highly stable Ag thin film where thermal agglomeration can be suppressed, by utilizing nanometer thick surface Al layers. Then we have confirmed that Al surface nanolayer deposited Ag films show a high optical reflectance as well as Ag single film. Here, the Al nanolayer was oxidized to be Al oxide nanolayer, being transparent in visible region, by natural oxidation in air. In the present study, we investigate durability of the Ag films with surface nanolayers under high humidity condition.

We prepared Ag single layer (150 nm), Ti (1, 3 -nm) / Ag films and Al (1, 3 -nm) / Ag films on glass substrate by rf magnetron sputtering in Ar discharge. In addition, vacuum evaporation method was also used for the preparation of Al (1, 3 -nm) / Ag films. A difference on degradation of the films by different fabrication methods was investigated. The samples were kept for 16 hrs in a chamber where temperature and humidity was set to 55°C and 90%RH, respectively.

After the test, agglomeration occurred in Ag single layer and optical reflectance was decreased. On the other hand, Ti or Al nanolayer covered Ag films kept smooth surface even after the test. The surface roughness observed using AFM was as small as 1.0 nm. As a result, we have found that both Al and Ti surface nanolayers can play significant role as protective layer under high humidity condition. However, Ti / Ag films showed a lower reflectance due to light absorption by TiO₂ layer formed on the surface, and the samples with Al surface nanolayer showed a higher optical reflectance.

By XPS analysis, very thin Ag sulfide formation was observed in Ag single film after the humidity test, but not in Ti or Al covered Ag films. This suggests very thin Al oxide or Ti oxide nanolayer prevented contact of Ag atoms and SO₂ gas in air. However, Ag signal was detected in the surface oxide layers, which indicates onset of outward diffusion of Ag atoms.

8:20am **DM+BI+SS-ThM2 Influence of the Electric Double Layer on Degradation of Materials**, *Dominik Dworschak, M. Valtiner*, Vienna University of Technology, Austria

Corrosion and adhesion science usually focuses on the solid side of a liquid/solid or solid/adhesive interface. However, the only some nanometer thick interface itself is the complex transition region which

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drives many important processes in corrosion and delamination. The electric double layer (EDL) is a key part of the interfacial region but remains mostly neglected as a potential key player in degradation processes. Here, we will demonstrate that the EDL has an important influence on the corrosion mechanism of passivating materials in the transpassive region (material dissolution at potentials where the passive film breaks down).

We utilize an electrochemical flow cell combined with an inductively coupled mass spectrometer (ICP-MS) to enable the in-situ study of the time-resolved release of elements into solution. This provides detailed insights into the nature of the passive and transpassive condition. As model systems, we use nickel based alloys. These are essential to modern industry and uniquely tailored for a wide range of applications, which rely on high corrosion and heat resistance. In particular, we polarized a series of Ni₇₅Cr₁₆Fe₉, Ni₈₆Cr₃Fe₉ as well as Ni₇₄Cr₁₆Fe₉Mo₁ model alloys in order to understand the effect of chromium concentration and molybdenum on transpassive dissolution

In the transpassive regime we can detect the presence of protective species of chromium and molybdenum on the surface. Unexpectedly, we can demonstrate significant corrosion resistance above a critical potential where the passive film breaks down. This is traditionally known as trans passive region with bulk dissolution of metal alloys. However, we find that the EDL forms a transient passivating solution side protective layer in the transpassive region – i.e. we characterize an electric double layer induced corrosion resistance, which solely – and surprisingly – lies in the structure of the solution side. This finding has general important implications for designing degradation resistance in highly corrosive environments.

8:40am **DM+BI+SS-ThM3 Key Issues for the Stability of Protective Surface Oxides, Philippe Marcus**, CNRS - Chimie ParisTech, France **INVITED**

This lecture will focus on a surface science approach of corrosion and protection of metals and alloys, with emphasis on the structure and growth of surface oxide layers, a central theme in corrosion science.

Understanding early stage oxidation of metal surfaces at atomic or nanometric scale is a key to a better design and an improved control of engineering metals.

The following topics will be addressed:

- Nanostructure of ultra-thin oxide layers (passive films) on metals,
- Early stage oxidation of stainless steels,
- Local electronic properties of passive films,
- Mechanisms of initiation of localized corrosion, with emphasis on the role of surface defects in localized attack leading to corrosion,

The data that will be presented are obtained by using *in situ* Scanning Tunneling Microscopy (STM), Scanning Tunneling Spectroscopy (STS), X-Ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ions Mass Spectrometry (ToF-SIMS) combined with electrochemical techniques and DFT calculations.

9:20am **DM+BI+SS-ThM5 Controlling and Observing Localized Dealloying Corrosion and Dissolution via Lateral Modification of Surfactant Inhibitor Layers**, S. Neupane, Hasselt University, Belgium; **Frank Uwe Renner**, IMEC vzw, Division IMOMECE, Belgium

Corrosion processes on metals and alloys may result in substantial degradation and loss of functionality. Mitigation strategies include alloy design, to allow for passivation, or the application of inhibitors to protect materials but they are often causing irreversible damage and potential catastrophic failure at more severe corrosion conditions. The ultimate understanding of the involved fundamental processes including the initial stages of corrosion attacks is still lacking, in particular on the important atomic and molecular scale. Surfactant inhibitors protect surfaces from corrosion by forming molecular layers or so-called self-assembled monolayers separating the material from the corrosive environment. Yet, with inhibitors *localized dealloying* takes place at higher electrochemical potentials [1]. To address the fundamental nature of the site of initiation of dealloying corrosion we have recently introduced different strategies for novel surface-science approaches [2]. On the one hand the inhibitor layer can be laterally modified by using a sequential application combining different steps of micro-contact printing and solution backfilling [3]. In consequence an array of artificial defects such as patch boundaries or displacements by overprinting using foreign impurity molecules can be obtained in a well-controlled way. On the other hand the molecular stability may be locally probed by molecular-scale force measurements employing AFM techniques. In the retract force curve molecular fishing events are eventually visible which can be correlated to the inhibition

efficiency. We here exemplify both aspects on noble metal model systems such as Cu-Au and more reactive surfaces including Cu-Zn and pure Cu. On Cu-Au surfaces initial dealloying pits are occurring along patch boundaries formed by sequential application of thiol inhibitors [4]. On Cu surfaces we applied different mercapto-benzimidazoles and could indeed link the observed layer stability with the actual corrosion behavior.

[1] A. Pareek et al., J. Am. Chem. Soc. 133 (2011) 18264–18271. [2] B. Shrestha et al., Faraday Discuss. 180 (2015), 191. [3] S. Neupane et al., Langmuir. 34 (2018) 66–72. [4] S. Neupane et al., submitted.

9:40am **DM+BI+SS-ThM6 In Situ Characterization of Interactions at Polymer/Metal Oxide Interfaces Under Aqueous Conditions by a Spectro-electrochemical Approach**, Sven Pletincx, Vrije Universiteit Brussel, Belgium; L.-L. Fockaert, J.M.C. Mol, Delft University of Technology, Netherlands; H. Terryn, T. Hauffman, Vrije Universiteit Brussel, Belgium

The mechanisms governing coating/metal oxide delamination are not yet fully understood, although strong and durable adhesive interactions at the interface are considered to be an important prerequisite for good coating durability. Achieving adequate adhesion strengths between an organic and inorganic system in various operating conditions is one of the complex challenges of interface engineering. However, obtaining local chemical information at this solid/solid interface is challenging, since common surface sensitive analysis techniques only operate under vacuum conditions, making it impossible to probe environmental effects *in situ*.¹

The analysis of this so-called buried interfaces is achieved by characterizing ultrathin polymer films onto a metal oxide substrate by ambient-pressure photoelectron spectroscopy (APXPS).² Here, we show that APXPS with a conventional X-ray source can be used to study the effects of water exposure on the interaction of acrylic coatings with aluminum oxide. This is done by making the polymer layer sufficiently thin to probe the interface non-destructively.

A *spectroelectrochemical* setup of *in situ* ATR-FTIR Kretschmann and Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) on a complementary model system is used to characterize and monitor the formed bonds at the metal oxide/polymer interface.³ A nanometer thin aluminum layer is sputtered on an IR transparent crystal, such that the IR signal reaches the oxide/polymer interface, obtaining a near-interface spectrum. This way, we have direct access to the interface, and the influence of an above-the-polymer electrolyte (i.e. H₂O) is probed. Simultaneously the protective properties and corrosion processes of the overall hybrid system are monitored by ORP-EIS.

This work shows that by using ultrathin films in combination with a set of recently developed techniques, it is possible to non-destructively and *in situ* probe interfacial changes in hybrid systems.

1. Watts, J. F. The Interfacial Chemistry of Adhesion: Novel Routes to the Holy Grail? *Adhes. Curr. Res. Appl.* 1–16 (2006). doi:10.1002/3527607307.ch1

2. Pletincx, S. *et al.* In Situ Characterization of the Initial Effect of Water on Molecular Interactions at the Interface of Organic/Inorganic Hybrid Systems. *Sci. Rep.* 7, 45123 (2017).

3. Pletincx, S. *et al.* In Situ Methanol Adsorption on Aluminum Oxide Monitored by a Combined ORP-EIS and ATR-FTIR Kretschmann Setup. *J. Phys. Chem. C* 122, 21963–21973 (2018).

11:00am **DM+BI+SS-ThM10 Design of Corrosion Resistant High Entropy Alloys**, Gerald Frankel, C.D. Taylor, W. Windl, The Ohio State University; J.R. Scully, University of Virginia; J. Locke, The Ohio State University; P. Lu, Questek Innovations **INVITED**

The corrosion resistance of a metal alloy is dictated by the exposure environment as well as the alloy structure, composition, and details of the surface condition such as the presence of a passive film. The design of new alloys with improved corrosion resistance must take all of these factors into account. As a result, the degrees of freedom in alloy design are so numerous that the standard process of trial and error is extremely lengthy, even using high throughput methods. This is particularly true for emerging materials such as high entropy alloys (HEAs) and bulk metallic glasses. The complexity of the corrosion process makes integrated computational materials engineering (ICME) for corrosion resistance very challenging. In this work we describe an approach for design of corrosion resistant alloys (CRAs) using ICME. The work has focused on HEAs because of the vast, multidimensional compositional and processing space associated with HEAs. The ultimate goal of CRA design is a combination of multiscale, multiphysics models that accurately describe the details of each of the controlling mechanisms and chemical/physical interactions in the

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degradation process. However, progress can be made using computational approaches coupled with empiricism. Calculation of Phase Diagrams (CalPhaD) methods are extremely useful in this regard. Furthermore, a number of relevant calculable parameters, such as metal-metal and metal-oxygen bond strength or chloride ion adsorption energies, can be used to create correlations with corrosion metrics that enable prediction of corrosion properties of alloys in previously unexplored compositional space. We will present the methodology used for the design of an extremely corrosion resistant HEA as well as a series of HEAs that are less resistant, but allow for the assessment of critical parameters controlling corrosion resistance in HEAs.

11:40am **DM+BI+SS-ThM12 Determination of Hydrogen in High Strength Steels using Scanning Kelvin Probe Force Microscopy**, *Ines Traxler, G. Schimo-Aichhorn*, CEST Competence Centre for Electrochemical Surface Technology, Austria; *A. Muhr, G. Luckeneder, H. Duchaczek, K.-H. Stellnberger*, voestalpine Stahl GmbH, Austria; *D. Rudomilova, T. Prosek*, University of Chemistry and Technology Prague, Czech Republic; *B. Lutzer*, CEST Competence Centre for Electrochemical Surface Technology, Austria; *D. Stifter, S. Hild*, Johannes Kepler University Linz, Austria

High-strength steels are important materials for the automotive industry. Due to their good formability and high strength they are used for the manufacture of light weight and fuel-efficient automotive parts. A disadvantage of high strength steels is their proneness to hydrogen embrittlement. Even small amounts of hydrogen can cause a deterioration of mechanical properties. Therefore, the effect of hydrogen on the steel microstructure is of great interest and it is important to study and visualize the effects and mechanisms of hydrogen in steels. For this purpose, Scanning Kelvin Probe Force Microscopy (SKPFM) is a promising technique for the investigation of hydrogen in the steel microstructure with a very good spatial resolution.

Hydrogen diffusion in different high-strength steels was investigated using SKPFM. Hydrogen entry at cut edges and coating defects was studied as well as the influence in the individual steel grains. The measurements were carried out with different salt solutions on the backside of CP1000 (complex phase), DP1000 (dual phase) and zinc coated DP1000 steels to induce corrosion and promote hydrogen entry into the steel. The permeating hydrogen was measured on the upper side of the sample by repeated surface scans and the effect on the contact potential difference (CPD) was studied. Furthermore, SKPFM measurements with different relative humidity were carried out, monitoring the effects of corrosion. Additionally, Scanning Kelvin Probe (SKP) measurements were done for comparison.

With SKPFM, the preferred diffusion pathways of hydrogen through the steel microstructure could be visualized as well as the effect of zinc coatings on hydrogen permeation.

12:00pm **DM+BI+SS-ThM13 Reflection Mode Interferometry for studying interfacial processes**, *Kai Schwenzfeier, P. Bilotto, M. Lengauer, C. Merola, H.-W. Cheng, M. Valtiner*, TU Wien, Austria

Molecular level processes at electrified solid|liquid interfaces play a critical role in corrosion and degradation processes. These include adsorption of ions, evolution of electrochemical double layers, oxidation/dissolution of metals, screening effects as well as liquid properties at an interface. However those processes/effects are notoriously hard to measure due to long integration times or too small probe with many available analysis techniques.

We refined Multiple Beam Interferometry (MBI) to enable time resolved in-situ and operando measurement of processes at solid|liquid interfaces in both transmission and reflection geometry. In this presentation dynamic interfacial processes such as changes of refractive indices in small (nanometer sized gaps), a micro-to-angstrom scale view into corrosion processes and surface oxidation, as well as specific and non-specific potential driven ion adsorption in aqueous solutions will be discussed in detail. We will relate these measurements to molecular resolution AFM imaging and force spectroscopy at solid|liquid interfaces.

2D Materials

Room A216 - Session 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA

Surface Chemistry, Functionalization, Bio, Energy and Sensor Applications

Moderator: Mark Edmonds, Monash University, Australia

2:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA1 Molecular Layers on Nanoporous Gold Electrodes**, *Elizabeth Landis*, College of the Holy Cross
Nanoporous gold presents a surface with high conductivity and surface area, which makes it an interesting platform for surface chemistry. However, the nanoporous gold surface lacks the functionality necessary for many applications including sensing. We have investigated self-assembled thiol-based monolayers and the electroreduction of diazonium-based salts to form aryl molecular layers on nanoporous gold. We use infrared spectroscopy and cyclic voltammetry to show that the molecular layer ordering and density depends on the functionalization method, and the underlying nanoporous surface impacts molecular ordering and electron transfer properties.

2:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA2 Thermotropic Liquid Crystal (5CB) on Two-dimensional Materials**, *Paul Brown*, American Society for Engineering Education; *S. Fischer, J. Kotacz, C.M. Spillmann, D. Gunlycke*, U.S. Naval Research Laboratory

Current means of redirecting light often rely on either bulky mechanical gimbals or non-mechanical diffractive elements. The former often suffer from wear and are susceptible to failure, while the latter may have significant optical power confined within side lobes. One promising non-mechanical approach that can overcome present limitations in beam redirection incorporates liquid crystal (LC) for continuous, refractive steering. Nematogens, the molecules comprising the LC in a nematic phase, support inherent anisotropic optical and dielectric properties that result from local ordering of single molecules. Recent research suggests the possibility of including two-dimensional materials to act as both an alignment layer and electrode to LC. This offers the possibility of further reducing device dimensions and device response time. Yet little research has focused on the ground state properties of a nematogen interfacing with the two-dimensional substrate. In this talk, we present density functional theory results of the electronic properties of a well-known nematogen (5CB) interacting with graphene, boron nitride, and phosphorene. We also discuss the influence of an introduced single vacancy on the electronic properties of the composite system. We find that 5CB on phosphorene offers the strongest binding of the considered nanosheets. Moreover, we observe qualitatively different band alignments, and focus in particular on type I, which prohibits free carrier transfer between the substrate and nematic LC. Lastly, we discuss the impact of single vacancies on the performance of two-dimensional materials to operate as both an alignment layer and electrode for LC-based applications.

This work has been supported by the Office of Naval Research, directly and through the U.S. Naval Research Laboratory.

3:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA3 Is it Possible to Achieve Intra-molecular Resolution with Ambient AFM?**, *Vladimir Korolkov*, Oxford Instruments-Asylum Research; *S.C. Chulikov, M. Watkins*, University of Lincoln, UK; *P.H. Beton*, The University of Nottingham, UK

Although achieving molecular resolution is now almost a routine across various SPM imaging modes, resolving the actual molecular structure at the atomic level has only been accomplished with NC-AFM in UHV often at low temperatures and with a functionalized probe. Of course, the ultimate goal in SPM is to resolve the chemical structure of a molecule identifying each atom.

In this work we are presenting an approach to achieve intra-molecular resolution on adsorbed molecules in the ambient at room temperatures with a standard AFM cantilever with unmodified tip. We have discovered that using a combination of higher eigenmodes and low oscillation amplitudes (~3-5Å) of a standard Si-cantilever routinely provides ultra-high resolution on adsorbed molecules on surfaces^{1,2} and bulk polymers³.

With this approach we have been able to observe both intra-molecular features and inter-molecular contrast in thin films of coronene and melem molecules on the surface of hexagonal boron nitride (hBN). In case of coronene, all six benzene rings have been resolved as well as underlying atomic lattice of hBN. Unlike coronene, melem forms molecular assemblies with square symmetry stabilized with in-plane strong hydrogen bonds between amino groups. We have observed a strong inter-molecular

contrast where the hydrogen bonds are expected to be. Similar to coronene, the observed intra-molecular contrast was associated with three triazine rings. We have used Probe particle model⁴ to simulate our experimental AFM images and found very good agreement between them. In fact, PPM allowed us a correct interpretation of melem square phase assembly.

Both systems were studied at room and elevated temperatures where we observed phase transitions leading to thermodynamically stable systems. The experimental results are in excellent agreement with density functional theory calculations.

We believe the proposed approach, yet still in its infancy, could potentially provide a pathway to unambiguous identification of molecules on surfaces in the ambient on standard AFM systems.

¹Korolkov et al., Nat. Chem., 2017

²Korolkov et al., Nat. Comm., 2017

³Korolkov et al., Nat. Comm., 2019

⁴Hapala et al., Phys. Rev. B 90, 085421

3:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA4 Tailoring Surface Properties via Functionalized Hydrofluorinated Graphene Compounds**, *Jangyup Son*, University of Illinois at Urbana-Champaign; *N. Buzov*, University of California at Santa Barbara; *S. Chen*, University of Illinois at Urbana-Champaign; *D. Sung*, Sejong University, Republic of Korea; *H. Ryu*, Seoul National University, Republic of Korea; *J. Kwon*, Yonsei University, Republic of Korea; *S. Kim, J. Xu*, University of Illinois at Urbana-Champaign; *S. Hong*, Sejong University, Republic of Korea; *W. King*, University of Illinois at Urbana-Champaign; *G.H. Lee*, Seoul National University, Republic of Korea; *A.M. van der Zande*, University of Illinois at Urbana-Champaign

Mixing compounds or alloys is an important process to tailor or enhance the intrinsic properties of materials such as chemical reactivity, mechanical strength, and electronic structure. In nanosystems, such as two-dimensional (2D) materials like graphene, transition metal dichalcogenides (TMDCs), and hexagonal boron nitride (hBN), where there is no distinction between the surface and the bulk, mixing of elements is also an important tool for tailoring the interaction of the material with its environment. A successful strategy for manipulating the chemical structures of 2D materials is the chemical functionalization of graphene with single elements such as H, O, N, and F. Yet, an even wider parameter space is possible by combining these functionalization species to produce ternary functionalized graphene compounds.

Here we present a new strategy for producing functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate tailored hydrofluorinated graphene (HFG) compounds via the sequential exposure of graphene to low-energy hydrogen plasma and xenon difluoride (XeF₂) gas. We demonstrate reversible switching of the surface between completely hydrogenated graphene (HG) and fluorinated graphene (FG) as well as the intermediate ratio between two extremes. Moreover, we demonstrate pattern the surface functionalization on a single chip into chemically distinct materials (graphene, FG, HG, and HFG compounds).

Finally, with these patterned structures, we demonstrated tailoring of the surface and electronic properties of the 2D materials. First, the patterned structures enable direct comparisons of the relative surface properties such as wettability and surface friction. Additionally, the electrical properties of functionalized graphene compounds showed unusual recovery of electrical conductance during the partial transformation of FG to HFG, due to initial removal of existing F adatoms when exposed to hydrogen plasma. This study opens a new class of 2D compound materials and innovative chemical patterning that can lead to atomically thin 2D circuits consisting of chemically/electrically modulated regions.

4:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA7 Towards Higher Alcohol Synthesis from Syngas on 2D material-based catalysts: A First-Principles Study***, *Tao Jiang, D. Le, T.S. Rahman*, University of Central Florida

Synthesis of higher alcohol from syngas has been of great interest owing to the limited petroleum resources and environmental concerns. Rational designing of cheap and efficient catalyst material for such synthesis is in great demand because of diminishing supply of the current state-of-the-art catalysts. Two dimensional (2D) materials are emerging with far-reaching potential for technical and industrial applications thanks to their unique properties, recent developments and improvement of production technologies. In this talk, we will discuss our recent work, based on first

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principles calculations, towards the unitization of 2D materials as catalysts for higher alcohol synthesis. In particular, defect laden hexagonal boron nitride (*dh*-BN) with N vacancies is excellent catalyst for hydrogenation of CO₂ towards ethanol formation, in the reaction pathway of which the crucial step for forming C₂ bond, i.e. reaction of adsorbed species CH₃* and CO* to form CH₃CO*, is exothermic with reasonably low activation barrier (0.68 eV). On the other hand, we also find single layer of MoS₂ functionalized with small Au nanoparticle to catalyze CO hydrogenation reaction towards ethanol formation. Among all the elementary reactions, the important steps are the reaction of an adsorbed CH₃* and a CO* molecule and the hydrogenation of acetyl to acetaldehyde (both are exothermic with activation barriers of 0.69 and 0.47 eV, respectively) to form C₂ species.[1] The results suggest that 2D materials are suitable candidates for higher alcohol synthesis. Full reaction pathways will be discussed together with results of Kinetic Monte Carlo simulations to shed light on the selectivity of the catalysts. Contact will be made with experimental data that validate our theoretical predictions.

[1] K. Almeida, K. Chagoya, A. Felix, T. Jiang et al, "Towards Higher Alcohol Formation using a single-layer MoS₂ activated Au on Silica: Methanol Carbonylation to Acetaldehyde", submitted

*Work supported in part by DOE Grant DE-FG02-07ER15842

4:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA8 Proton Conductivity Properties of Electrospun Chitosan Nanofibers, Woo-Kyung Lee, J.J. Pietron, D.A. Kidwell, J.T. Robinson, C.L. McGann, S.P. Mulvaney, U.S. Naval Research Laboratory**

A major challenge of the 21st century will be to establish meaningful two-way communication between biology and electronics. The study of protonics, devices that mimic electronics but pass protons instead of electrons, seeks to bridge this gap. Protonic conductive materials (PCMs) are essential elements of these devices and we have demonstrated significant improvement in conductivity for chitosan PCMs when deposited as electrospun nanofibers. The observed improvements stem from both enhanced molecular alignment and from chemical doping due to the electrospinning carrier fluid, trifluoroacetic acid (TFA). We deposited electrospun chitosan nanofibers over palladium protodes and then used the helium ion microscope to isolate single nanofibers for detailed study. We observed that single chitosan nanofibers are strongly doped by TFA with x-ray photoelectron spectroscopy demonstrating extensively protonated nitrogen functionality. With the isolated, single chitosan nanofibers we observed that water uptake, fiber/electrode contact area, and doping concentration are critical parameters of protonic device performance and lead to increased conductivity (*i.e.* low resistivity). The average resistivity of single chitosan nanofibers is $6.2 \times 10^4 \Omega\text{-cm}$, approximately two orders of magnitude lower than the resistivity of cast chitosan PCMs (cast from acetic acid solutions not TFA). We have observed excellent agreement between theoretical models and experiment results that explore each of the contributions to the improved conductivity. In addition, the fabrication and measurement of ionic field-effect transistor of single chitosan fiber using conductive atomic force microscope will be discussed.

5:00pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA9 Sensor for Breath and Skin Diagnostics, Pelagia I Gouma, The Ohio State University**

Resistive gas sensors have received a bad reputation of being largely non-selective.

Our work has produced a crystallo-chemical model for selective gas sensing by polymorphic

metal oxides. The reaction-based and ferro-electric poling sensing mechanisms are discussed

in detail. Novel processing methods to produce the respective nano sensors are presented along

with the device fabrication for the non-invasive diagnosis of gaseous biomarkers in human

and animal breath or skin. This sensor technology is expected to revolutionize medical diagnostics.

5:20pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA10 Symmetry Controlled Adsorption of Diodobenzene on MoS₂, Zahra Hooshmand, University of Central Florida; P. Evans, P.A. Dowben, University of Nebraska - Lincoln; T.S. Rahman, University of Central Florida**

In a joint experimental and theoretical study, we have uncovered evidence of the importance of symmetry in the adsorption of the isomers of diiodobenzene on MoS₂(0001). The intensity ratio of iodine to molybdenum

measured, as a function of exposure for different isomers of the diiodobenzene, show that while for ortho (1,2-) and para (1,4-) diiodobenzene the rate of adsorption at 100 K is very low, that for meta (1,3-) diiodobenzene is considerably more facile. We have applied dispersion corrected density functional theory-based calculations to understand the subtleties in the electronic structure and geometry of adsorption of these diiodobenzene isomers on MoS₂(0001). All three isomers are found to weakly chemisorb with the same binding strength as well as adopt similar configurations. The calculated electron affinity of the three molecules also do not show a specific trend that would verify experimental data. However, analysis of the frontier orbitals indicate that those of 1,3-diiodobenzene are strongly affected by interactions with MoS₂, while that of the other two isomers remain unchanged. Our results show that symmetry is the identifying factor in these adsorption characteristics. The results of frontier orbitals analysis confirm that for adsorption of (1,2-) and (1,4-) diiodobenzene a reduction in the symmetry of the adsorbent is needed. To further validate our conclusions, we compare the above results with that of the adsorption of the diiodobenzene isomers on defect-laden MoS₂(0001).

* Work support in part by DOE grant DE-FG02-07ER15842

5:40pm **2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA11 Mechanistic Understanding of the CO Hydrogenation Reaction on Defect Engineered 2D-TaS₂ and 2D-MoS₂ Catalysts, Mihai Vaida, University of Central Florida**

Due to global energy demands, investigation of catalytic reaction mechanisms on novel catalytic materials that can lead to efficient production of storable fuels from sustainable inputs is of central importance. In this contribution the adsorption of CO and H₂ molecules, as well as the CO hydrogenation reaction are investigated on defect engineered two dimensional (2D) TaS₂ and MoS₂. Crystalline 2D-TaS₂ and 2D-MoS₂ with surface area of 1 cm² are synthesized via a multistep process based physical vapor deposition on Cu(111). The surface composition, morphology, and electronic structure are investigated via Auger electron spectroscopy, low energy electron diffraction, scanning tunneling microscopy, scanning tunneling spectroscopy, and photoemission spectroscopy. The interaction of the molecules with the surface and the catalytic reaction mechanisms are investigated via temperature programmed desorption/reaction. No catalytic reactions have been observed on crystalline 2D materials. However, an enhanced catalytic activity is observed after the generation of sulfur vacancies via Ar sputtering. The CO hydrogenation on TaS₂ occurs on low coordinated Ta atoms through the formation of formyl radical (HCO) and formaldehyde (HCOH). On 2D-MoS₂, the CO hydrogenation also occurs on low coordinated Mo atoms. However, in this case the formyl radical splits to form methyldyne radical (CH), which subsequently react with other CH radical to produce acetylene (C₂H₂).

Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM1+BI+SS-ThA

Low Fouling Interfaces and Environmental Degradation

Moderator: Axel Rosenhahn, Ruhr-University Bochum, Germany

2:20pm **DM1+BI+SS-ThA1 Utilizing Experimental and MD Simulation Approaches in the Understanding and Design of Low Fouling Interfaces, Paul Molino, University of Wollongong, Australia** INVITED

Biofouling is a ubiquitous problem for a diverse suite of industries, impacting the functionality of materials and devices. Diverse approaches taken in the design of materials and interfaces to prevent microbial fouling often rely on atomic and molecular scale processes, however the fundamental mechanism/s underlying these processes, and their mode of action, in many cases continue to elude researchers. Highly hydrophilic chemistries such as polyethylene glycol and zwitterion-based chemistries, have long been used to generate interfaces that prevent biological interactions at surfaces. Such surface chemistries have been proposed to function through a combination of molecular water organisation and steric repulsion at the interface. Experimental approaches have confirmed the presence of hydration layers associated with hydrophilic polymer-based surfaces, yet the fundamental mechanisms underlying their capacity to inhibit surface fouling, and how such hydration layers differ from equally hydrophilic interfaces that do not prevent surface fouling is still unclear. Molecular dynamic (MD) simulations have gone some way to provide critical insights into their respective mechanism/s of action, however experimental approaches capable of adequately resolving features at a

suitable spatial resolution to corroborate and build on these models have been lacking. Herein I will present a highly biofouling resistant coating composed of silica nanoparticles functionalised with a short chain hydrophilic silane. To understand the interfacial environment at the hydrated nanoparticle surface, frequency modulation – atomic force microscopy was used to provide sub-atomic resolution of the water structuring about the nanoparticle interface, which we validate using all-atom molecular dynamic simulations that strikingly predict similar structures of water layers on the original and ultralow fouling surfaces. The convergence of experimental and modelling data reveals that suitably spaced, flexible chains with hydrophilic groups interact with water molecules to produce a connective, *quasi-stable* layer, consisting of dynamic interfacial water, that provides a basis for antifouling performance of ultrathin, hydrophilic surface chemistries. This approach provides a road map for the future development and optimisation of interfacial chemistries and materials designed to combat biofouling and biodegradation.

3:00pm DM1+BI+SS-ThA3 Study of Environmental Exposure Effects on Pristine and DC Magnetron Sputtering Metallic Coated 3D Printed Polymers, D. Mihut, Arash Afshar, P. Chen, Mercer University

Three dimensional printing is a promising technique for producing complex geometries and high precision structures from different types of materials. The technique is particularly attractive for polymeric materials due to the cost effectiveness; however when compared to other manufacturing techniques the resulting structures have low mechanical properties and low performance as exposed to harsh environmental conditions. ABS (acrylonitrile butadiene styrene) and PLA (polylactic acid) are common thermoplastic polymers used for many applications (e.g. electrical and electronic assemblies, medical devices, implants, toys). For this research, the ABS and PLA specimens for tensile and flexural testing were 3D manufactured according to standards and their mechanical properties were tested using hardness tester, and Mark-10 tensile testing equipment. In order to simulate outdoor environmental conditions while avoiding the uncertainties associated with it, specimens were exposed to controlled environmental chamber. Accelerated exposure was performed using a UV radiation/condensation (Q-Lab QUV/basic) accelerated weathering tester. ABS and PLA samples were exposed to UV radiation, high temperature and moisture cycles for different time intervals. Some ABS samples were coated with optically thick metallic materials (silver and copper) using high vacuum DC magnetron sputtering deposition system and were later exposed to UV radiation, high temperature and moisture cycles using same conditions as for un-coated samples. The surface and cross section morphology of samples and the adhesion of metallic layers to the polymer substrates were examined using scanning electron microscopy and laser scanning microscopy. The crystalline structure of the metallic coatings was analyzed using X-ray Diffraction technique. The mechanical properties were characterized using flexural and hardness tests over the exposure time. The metallic thin films improved the surface resistance of the substrate materials and enhanced the mechanical behavior of samples exposed to harsh environmental conditions.

3:20pm DM1+BI+SS-ThA4 Reaction Mechanism of Chloride-induced Depassivation of Oxide Films: a Density Functional Theory Study, Q. Pang, H. DorMohammadi, K. Oware Sarfo, P.V. Murkute, Y. Zhang, O.B. Isgor, J.D. Tucker, Líney Árnadóttir, Oregon State University

A protective iron oxide film (passive film) forms on the surface of iron in alkaline environment, such as in reinforced concrete. Chloride and other aggressive ions can cause the breakdown of the passive film (depassivation) in the same environment, leading to active corrosion. The mechanism of the Cl-induced depassivation is studied on flat and stepped α -Fe₂O₃ (0001) surfaces because α -Fe₂O₃ has been suggested to be one of the dominant oxides in the outer layer of the passive film.

The oxidation state of the surface metal atoms plays an important role in Cl-surface interactions and depassivation. Cl binds more strongly to metal atoms at lower oxidation state and these adsorption sites can facilitate higher local coverage. Defect sites, such as on a step edge or next to a O vacancy have lower oxidation states, suggesting an important role of defects in the depassivation process. Two main mechanisms of depassivation have been proposed in the literature, the point defect model that proposes a depassivation through Cl enhanced Fe vacancy formation on the surface and void formation at the metal oxide/metal interface, and the ion exchange model, which proposes a depassivation mechanism through subsurface Cl. Our studies of the thermodynamics of Cl ingress into the passive film, Fe vacancy formation, and bulk vacancy stability all support the point defect model for iron oxide. The initial stages of Cl-

induced depassivation are proposed through a combination of reactive force field molecular dynamics simulations and DFT calculations.

Fundamental Aspects of Material Degradation Focus Topic Room A212 - Session DM2+BI+SS-ThA

Fundamentals of Catalyst Degradation: Dissolution, Oxidation and Sintering

Moderator: Gareth S. Parkinson, TU Wien, Austria

4:00pm DM2+BI+SS-ThA6 Stability Challenges in Electrocatalysis, Serhiy Cherevko, Forschungszentrum Jülich GmbH, Germany INVITED

Many industrially important electrochemical energy conversion technologies, such as electrolysis and fuel cells, rely on expensive noble metal electrocatalysts to accelerate reactions, and thus, improve energy conversion efficiency. Despite their relatively high stability, even noble metals are not completely immune. Indeed, the latter fact represents a considerable challenge in the wide-spread commercialization of electrolyzers and fuel cells. Electrocatalyst or support corrosion, particle agglomeration and detachment, Ostwald ripening, structural and morphological changes are just a few examples of possible degradation processes.¹ These processes clearly illustrate the level of complexity one has to deal with in order to understand and circumvent degradation in real devices. Thus, it is difficult to imagine modern electrocatalysis research without advanced analytical tools. In this talk I will demonstrate that the application of on-line inductively coupled plasma mass spectrometry, on-line electrochemical mass spectrometry, and identical location transmission electron microscopy in electrocatalysis research can assist in clarifying the mechanisms leading to degradation. As some representative examples I will show degradation of the state-of-the-art and advanced platinum based catalysts in fuel cells and iridium based catalyst in water electrolysis.²⁻⁴ Time will also be devoted to discussing application of alternative non-noble metal catalysts in the energy conversion technologies and their stability. Finally, stability in other electrocatalytic systems, e.g. photo-electrochemical water splitting or carbon dioxide reduction will be touched.

Literature:

- 1 Cherevko, S. *Current Opinion in Electrochemistry***8**, 118-125 (2018).
- 2 Cherevko, S. *et al. Nano Energy***29**, 275-298, (2016).
- 3 Kasian, O. *et al. Angewandte Chemie***57**, 2488-2491 (2018).
- 4 Geiger, S. *et al. Nature Catalysis***1**, 508-515 (2018).

4:40pm DM2+BI+SS-ThA8 Self-limited Growth of an Oxyhydroxide Phase at the Fe₃O₄(001) Surface in Liquid and Ambient Pressure Water, Florian Kraushofer, TU Wien, Austria; F. Mirabella, TU Wien, Austria, Germany; J. Xu, J. Pavelec, J. Balajka, M. Müllner, N. Resch, Z. Jakub, J. Hulva, M. Meier, M. Schmid, U. Diebold, G.S. Parkinson, TU Wien, Austria

Atomic-scale investigations of metal oxide surfaces exposed to aqueous environments are vital to understand degradation phenomena (e.g. dissolution and corrosion) as well as the performance of these materials in applications. Here, we utilize a new experimental setup for the UHV-compatible dosing of liquids to explore the stability of the Fe₃O₄(001)-(√2 × √2)R45° surface following exposure to liquid and ambient pressure water, using low energy electron diffraction (LEED), x-ray photoemission spectroscopy (XPS) and scanning tunnelling microscopy (STM).

Short-time exposure of the surface to clean H₂O results in hydroxylation of the surface, which is not observed in UHV. After longer exposure times, we observe lifting of the (√2 × √2)R45° reconstruction with LEED and stronger hydroxylation of the surface with XPS, in agreement with previous reports. However, scanning tunnelling microscopy (STM) images reveal a more complex situation than simply reverting to a bulk-truncation, with the slow growth of an oxyhydroxide phase, which ultimately saturates at approximately 40% coverage. We conclude that the new material contains OH groups from dissociated water coordinated to Fe cations extracted from subsurface layers, and that the surface passivates once the surface oxygen lattice is saturated with H because no further dissociation can take place.

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5:00pm **DM2+BI+SS-ThA9 The Impact of W on the Early Stages of Oxide Evolution for Ni-Cr Alloys**, C. Volders, V.A. Avincola, University of Virginia; I. Waluyo, Brookhaven National Laboratory; J. Perepezko, University of Wisconsin - Madison; **Petra Reinke**, University of Virginia

Ni-Cr alloys are highly coveted as they exhibit superior corrosion resistance due to the formation of a passive chromia film which helps protect the underlying alloy from degradation. The properties of this system are further enhanced through the addition of minor alloying elements such as Mo or W. For example, Mo is known to reduce catastrophic events such as pitting and crevice corrosion, thereby enhancing overall corrosion resistance. The ideal composition for technical Ni-Cr alloys has been optimized over many decades, however, the mechanistic understanding for the role of alloying elements such as Mo and W has not been fully developed. The primary objective of this work is to formulate a better mechanistic understanding of how the addition of W impacts the early stages of oxidation for this system and eventually use this information for further improvement of Ni-Cr alloys.

To achieve our goal, a series of oxidation experiments with the direct comparison between Ni-15Cr and Ni-15Cr-6W (weight percent) samples were performed and analyzed with the use of X-ray photoelectron spectroscopy (XPS). The first set of experiments employed an *in-operando* XPS approach where the modulation of alloy and oxide composition and bonding was observed over an extended period of time delivering a detailed view of the reaction pathways. The key results from this work include the observation of Cr surface segregation in the alloys prior to oxidation, which contributes to a rapid nucleation of Cr oxide species in the first reaction steps. The more intriguing result was the addition of W to the alloy resulted in a near complete suppression in the formation of Ni oxide, while further enhancing the formation of a pure chromia phase, which has been attributed to the addition of W increasing the supply of Cr to the surface and will be discussed.

A second series of XPS experiments focus on oxidation as function of crystallographic orientation of individual, large grains for Ni-15Cr and Ni-15Cr-6W. The differences in atom density and surface energies as a function of orientation lead us to expect significant differences in reactivity which will impact passivation and oxide performance. This has been demonstrated for aqueous corrosion of NiCr and NiCrMo alloys by Scully et al. *J. Phys. Chem. C*, **2018**, 122 (34), 19499-19513, and our work is complementary for thermal oxidation studies. In this work, Ni-15Cr and Ni-15Cr-6W samples were thermally oxidized and we will present and discuss the difference in oxidation products for various grain orientations for both samples.

5:20pm **DM2+BI+SS-ThA10 The Stability of Platinum in Non-aqueous Media**, J. Ranninger, S. Wachs, J. Möller, K. Mayrhofer, **Balázs Berkes**, Forschungszentrum Jülich GmbH, Germany

Many basic reactions in electrochemistry, like the hydrogen oxidation reaction, oxygen reduction reaction, water oxidation or CO₂ reduction reaction has been thoroughly studied in aqueous electrolytes. To these fundamental studies well defined experimental conditions have been chosen: smooth or single crystal electrodes with known surface structures, ultrapure electrolytes and very clean experimental apparatus. In many respects electrocatalysis in organic solvents is much less advanced than its understanding in aqueous systems.

The example of LIBs shows us, however, clearly how much potential of non-aqueous electrochemistry holds, in this particular example for the development of energy storage devices. Other important and possible technical applications are new type of batteries, electro-organic synthesis including electrochemical reduction of CO₂, electrodeposition, supercapacitors or electrochemiluminescence.

Stability of electrochemical systems is a particularly important question in electrocatalysis. No matter if it is a fuel cell, a battery, a supercapacitor, a construction subject to corrosion or an electrode used for synthesis, economic considerations require a certain lifetime of these systems. Therefore, it is also important to understand electrocatalysis especially the aspect of stability in non-aqueous electrolytes. To this end very sophisticated, often *in situ* and real-time analysis methods are required. In this work we show a powerful approach to study dissolution phenomena in non-aqueous electrochemical systems on the example of platinum.

Platinum is often considered to be a model electrode and catalyst material. This metal is probably the most thoroughly studied one in electrochemistry, however, it still shows many interesting yet not well understood features. This is also true for the stability of the metal during potential cycling. The electrochemical stability window of organic

electrolytes is usually much higher than that of water enabling the simultaneous cycling and downstream analysis of dissolution in a higher potential range. As a result, even the electrochemistry of platinum shows hitherto unveiled phenomena regarding its dissolution mechanism especially when using electrolytes with ultra-low (1 ppm) water content. In this work, we focus on the effect of water, anions, cations and organic solvent molecules on the anodic and cathodic dissolution behavior of platinum. To demonstrate the benefits of this novel method on the field of non-aqueous electrochemistry the stability of other non-aqueous systems will be discussed shortly, too.

5:40pm **DM2+BI+SS-ThA11 Stabilizing Transparent Conductive Oxides as a Route to Long-Lived Thin Film Photovoltaics: A Case Study in CIGS**, N.C. Kovach, Colorado School of Mines; R. Matthews, E.B. Pentzer, Case Western Reserve University; L. Mansfield, National Renewable Energy Laboratory; T.J. Peshek, NASA Glenn Research Center; **Ina Martin**, Case Western Reserve University

Degradation of the aluminum-doped zinc oxide (AZO) top contact is a known failure mode in Cu(In,Ga)Se₂ (CIGS) solar cells. The degradation of the AZO can be observed in device and module current-voltage characteristics as an increase in series resistance and decrease in fill factor. Due to its low cost and earth abundance, AZO is a good choice for the TCO in thin-film solar cells. However, it has one of the higher degradation rates of TCOs under damp heat stress. 3-aminopropyltriethoxysilane (APTES) was used to modify the AZO top contacts in CIGS solar cells. Results demonstrate that the application of the nm-scale modifier mitigates AZO degradation in damp-heat exposure, and further, arrests the degradation of the full CIGS device.

APTES modification of thick (~0.8 μm) AZO films significantly impedes the electrical degradation of the material caused by DH exposure, without significantly affecting the initial optical, electrical, or structural properties of the AZO films. Upon 1000 h of DH exposure, resistivity of both systems increased and can be attributed only to decreased mobility, as carrier concentration was consistent. APTES modification slowed the increase in AZO resistivity over 1000 h of DH exposure; however, the protective nature of APTES modification became critical after 1500 h. At this extended exposure time, macroscopic degradation was observed only for bare AZO including pitting and delamination and was accompanied by an increase in resistivity and decrease in carrier concentration. X-ray photoelectron spectroscopy (XPS) data show that the APTES layer stabilizes the oxygen binding environment of the AZO surface, suggesting that covalent passivation of AZO surface sites by silanization essentially “caps” reactive moieties, thereby improving the stability of the material.

Bold page numbers indicate presenter

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2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA11, **29**

Vallée, C.: AS+BI+RA-TuM13, 7

Valtiner, M.: BI+AS-MoA9, **5**; BI+AS-TuA1, 12; DM+BI+SS-ThM13, 27; DM+BI+SS-ThM2, 25

van der Heide, P.A.W.: RA+AS+BI-WeA2, 22

van der Zande, A.M.:

2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA4, 28

Vandervorst, W.: RA+AS+BI-WeA2, 22

Vanleenhove, A.: RA+AS+BI-WeA2, 22

Vargas-Giraldo, S.: BI+AS-TuM12, 9

Villaggio, G.: BI+AS-TuA9, 13

Volders, C.: DM2+BI+SS-ThA9, 31

— W —

Wachs, S.: DM2+BI+SS-ThA10, 31

Walker, A.V.: AS+BI+RA-TuM4, 6

Waluyo, I.: DM2+BI+SS-ThA9, 31

Wanka, R.: BI+AS-WeM1, 19; BI+AS-WeM2, 19; BI+AS-WeM5, **19**

Watkins, M.:

2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA3, 28

Weidner, T.: BI+AS-TuA2, 12; BI+AS-TuA7, 13

Weigang, A.: BI-TuP1, 15

Werner, C.: BI+AS-TuM6, 9; BI-TuP7, 16

White, L.: BI-TuP1, 15

Wilkesman, J.: BI+AS-TuA8, **13**

Williamson, T.: AS+BI+RA-TuM1, **6**

Windl, W.: DM+BI+SS-ThM10, 26

Wortmann, M.: AS+BI+RA-TuM12, **7**

— X —

Xu, J.: 2D+AS+BI+HC+MN+NS+PS+SS+TL-ThA4, 28; DM2+BI+SS-ThA8, 30

— Y —

Yang, C.: BI+AS-TuM13, **9**

Yu, W.: BI+AS-WeM1, 19

Yu, X.-Y.: BI+AS-TuM13, 9; BI+AS-TuM3, 8

— Z —

Zauscher, S.: BI+AS+NS-MoM1, 2; BI+AS+NS-MoM6, **3**

Zborowski, C.: RA+AS+BI-WeA2, 22

Zeller, P.: CA+2D+AS+BI+NS-ThM4, 24

Zhang, Y.: AS+BI+CA+LS-TuA11, **12**; DM1+BI+SS-ThA4, 30

Zhang, Y.C.: BI+AS-TuM3, **8**

Zhao, S.: BI+AS+NS-MoM6, 3

Zhu, Z.H.: AS+BI+CA+LS-TuA11, 12; BI-TuP5, **16**

Zimmermann, R.: BI+AS-TuM6, 9; BI-TuP7, 16