

# Thursday Morning, October 22, 2015

## Applied Surface Science

Room: 212D - Session AS-ThM

### Practical Surface Analysis III: Multiple-technique Problem-solving and Structure-property Correlations

**Moderator:** Michaeleen Pacholski, The Dow Chemical Company, Daniel Gaspar, Pacific Northwest National Laboratory

#### 8:00am AS-ThM1 Correlation of Substrate Surface Chemistry and Roughness to Adhesion of Pressure Sensitive Adhesives, *Michaeleen Pacholski, T. Powell, D. Keely, W.B. Griffith*, The Dow Chemical Company

This investigation focuses on the surface chemistry and roughness of substrates and the relationship to adhesion. We discuss the variability in surface chemistry and roughness of materials all nominally identified as the same material. For example, high density polyethylene (HDPE) is a common material used for bottles as well as a preferred low energy substrate for adhesion testing. However, there are several types of surface treatments used to increase adhesion. Surface roughness can also affect adhesion. We have compared corrugated cardboard surfaces and the influence of surface roughness on adhesion.

#### 8:20am AS-ThM2 Surface and Interface Studies of Ultra-Low Wear (ULW) PTFE/Alumina Polymer Composites, *Lei Zhang, G.S. Blackman, C.P. Junk, L. Amspacher, K.G. Lloyd, J.R. Marsh, D.J. Kasprzak*, DuPont Central Research and Development

In the past few years, polymer composites of polytetrafluoroethylene (PTFE) and alumina particles have attracted a lot of interest as a promising Ultra-Low Wear (ULW) material. It has been discovered that by adding a small amount of alumina additive (<5wt%) to PTFE, the wear rate of the PTFE is enhanced dramatically by over four orders of magnitude. Although this polymer composite system has shown its uniqueness and importance in the tribological research, the tribochemical mechanism has not been well understood.

To fully understand the chemistry that occurs during the tribology/wearing, it requires the precise design of experiments as well as applying integrated techniques to study the tribochemical process. In our studies, we investigated the tribochemical products by studying the unique chemistry of the transfer film formed at the composite and stainless steel interfaces during wearing. XPS, FTIR, and ToF-SIMS techniques have been applied to determine the chemistry of these tribochemical products as a function of number of sliding cycles. These characterization techniques have allowed us to understand the ultralow wear behavior and help to develop a conceptual framework for the ultralow wear material system.

#### 8:40am AS-ThM3 Investigation of Increased Glide Force of Prefilled Syringes Using Multiple Analytical Techniques, *Xia Dong, Z. Xiao, C.A.J. Kemp, G.H. Shi*, Eli Lilly and Company

Time-based glide-force changes in pre-filled syringes built into autoinjector systems can lead to negative patient experience issues and dose accuracy problems. The long term performance of prefilled syringe systems is examined during stability testing study when monoclonal antibody solutions are stored at various temperatures for given time periods. Multiple parameters including lubricant amount, lubricant distribution, and surface chemistry contribute to friction between the plunger and barrel and consequently the glide force. Therefore, it is important to understand the impact of storage conditions on lubricant characteristics and surface properties so that the desirable long term performance can be achieved.

In the current study, a monoclonal antibody solution was filled in glass syringes coated with silicone lubricant. Increased glide forces were observed from syringes stored at 25 °C, comparing to those stored at 5 °C. Multiple analytical techniques, including ellipsometry, ICP-OES, contact angle, XPS and TOF-SIMS were utilized to characterize lubricant and surface properties of syringe interior surfaces to understand the root cause of undesirable glide force changes.

#### 9:00am AS-ThM4 Degradation of Polypropylene Surgical Mesh: An XPS, FTIR, and SEM Study, *Bridget Rogers*, Vanderbilt University, *R.F. Dunn*, Polymer & Chemical Technologies, LLC., *S.A. Guelcher*, Vanderbilt University

Polypropylene mesh has been used to surgically treat stress urinary incontinence and has shown promising short-term results. However, serious complications have been associated with longer term implanted meshes. We

hypothesize that these complications are due to oxidative degradation of the mesh brought about by reactive oxygen species that are released by adherent macrophages on the surface of the polypropylene.

Polypropylene is known to oxidize through a stable hydroperoxide (-COOH) intermediate, followed by chain scission and formation of a carbonyl (-C=O) end group. Oxidation of polypropylene leads to a reduction in molecular weight, embrittlement, cracking, and eventually fracture and fragmentation. An *in vitro* study was performed to study the oxidation of polypropylene surgical mesh in a model environment that simulates conditions the mesh would experience in the body. Samples cut from three commercially available surgical devices produced by two manufacturers and polypropylene control samples were placed in an oxidizing medium consisting of 20% H<sub>2</sub>O<sub>2</sub> and 0.1 M CoCl<sub>2</sub>.

Samples were placed in the oxidizing medium and were incubated at 37 °C on a shaker for up to 6 weeks. The oxidizing medium was replaced every 3 to 4 days. Six samples were removed every week, washed in DI water, and dried. XPS and FTIR were used to analyze the samples for the presence of hydroperoxide and carbonyl species. SEM micrographs were acquired at 0, 4, and 5 weeks of oxidation.

We will present the XPS, FTIR, and SEM analytical results of the samples from this *in vitro* study. These results show that the anti-oxidants in the polypropylene mesh delay, but do not inhibit oxidation. SEM micrographs show surface pitting and flaking of samples exposed to the oxidizing medium.

#### 9:20am AS-ThM5 ASSD 30th Anniversary Lecture: Evolution of the Nature and Application of Surface Analysis: Challenges, Pitfalls, and Opportunities Past, Present and Future, *Donald Baer*, Pacific Northwest National Laboratory **INVITED**

Over the past 30 years there has been a remarkable range of advances in the ability to understand the nature of many types of important surfaces and interfaces. X-ray photoelectron spectroscopy (XPS) has become nearly essential for characterizing many types of materials, verifying the quality of synthesis methods and understanding interactions of these materials in many environments and applications. This has become possible because of major improvements in instrumentation including stability, reproducibility, increases in spatial resolution, increases in count rate, major improvements in the ability to analyze insulating samples, digital control of instruments and advances in the ability to process, model and analyze the data. For Auger electron spectroscopy (AES) similar advances have occurred, with spatial resolution being an obvious differentiator. In the area of Secondary Ion Mass Spectrometry, the major excitement has been related to the evolution of new primary and sputter beams with Bucky ball and cluster sources. Thirty years ago scanning probe methods were just beginning to appear; now they serve as critical tools for many types of studies.

In spite of the significant progress, many important materials information needs remain, providing opportunities for continued evolution of traditional surface analysis tools and the development and applications of other methods. These might be framed in the context of some "what if" questions that are not out of the range of the possible. What if we could monitor in real-time the evolution of surfaces and buried interfaces (and the actual compositional and chemical information at those interfaces) in "operational" environments? What if we could obtain quantitative compositional and chemical information at the resolution of an AFM? What if micro-technology could be used to create an XPS unit that produced quality data and operated without or with only trivial need for vacuum? What would be possible if NMR could be easily used to quantitatively characterize surfaces, interfaces or individual particles? Examples of progress along these directions will be described. All indications are that the next 30 years will be as dynamic and productive as the past 30 years, if not more so.

#### 11:00am AS-ThM10 Unraveling the Dynamic Nature of Mixed-Metal Oxides Nanocatalysts: An *In Situ* Multiple-Technique Approach, *Dario Stacchiola*, Brookhaven National Laboratory **INVITED**

Catalysts have traditionally been characterized before or after reactions and analyzed based on static representations of surface structures. It is shown here how dynamic changes on a catalyst's chemical state and morphology can be followed during a reaction by a combination of *in situ* microscopy (AP-STM) and spectroscopy (AP-XPS and AP-IRRAS). In addition to determining the active phase of the catalyst by *in situ* methods, the presence of weakly adsorbed surface species or intermediates generated only in the presence of reactants can be determined, allowing in turn the comparison of experimental results with first principle modeling of specific reaction mechanisms. Three reactions are used to exemplify the approach: CO oxidation (CO + 1/2O<sub>2</sub> → CO<sub>2</sub>), water gas shift reaction (CO + H<sub>2</sub>O → CO<sub>2</sub>

+H<sub>2</sub>) and methanol synthesis (CO<sub>2</sub> + 3H<sub>2</sub> → CH<sub>3</sub>OH + H<sub>2</sub>O). During CO oxidation, the full conversion of Cu<sup>0</sup> to Cu<sup>+2</sup> deactivates an initially outstanding catalyst. This can be remedied by the formation of a TiCuO<sub>x</sub> mixed-oxide that protects the presence of active partially oxidized Cu<sup>+</sup> cations. We also show the switch from a redox mechanism on Cu(111) to a more efficient associative mechanism pathway for the WGS at the interface of ceria nanoparticles deposited on Cu(111) [1]. Similarly, the activation of CO<sub>2</sub> at the ceria/Cu(111) interface allows its facile hydrogenation to methanol [2]. Our combined studies emphasize the need of searching for optimal metal/oxide interfaces, where multifunctional sites can lead to new efficient reaction pathways.

[1] *Angew. Chem. Int. Ed.* **52**, 5101–5105 (2013)

[2] *Science*, **345**, 546-550 (2014)

11:40am **AS-ThM12 Correlation between Chemistry, Optical Properties, and Environmental Stability of DC Sputtered Rhenium Oxides**, Neil Murphy, Air Force Research Laboratory, L. Sun, General Dynamics Information Technology, J.G. Jones, Air Force Research Laboratory, J.T. Grant, General Dynamics Information Technology

Thin films of rhenium oxide (<150 nm) are deposited using magnetron sputtering employing a rhenium cathode within an argon-oxygen atmosphere. Throughout the deposition process, the working pressure is maintained at a constant level of 1.33 Pa as the oxygen content is varied from 0% to 80% in increments of 10%. As the oxygen content is varied, the extinction coefficient, *k*, of the deposited layers is monitored via *in situ* ellipsometry. *In situ* ellipsometry is used to identify absorption features specific to ReO<sub>3</sub>, including the characteristic reduction of *k* brought on by the optical band gap at 310 nm as well as the onset of intraband absorption above 540 nm. *In situ* ellipsometry results indicate that films deposited at oxygen levels of 50% and 60% have respective *k*<sub>450</sub> values of 0.6 and 0.25, characteristic of ReO<sub>3</sub>. Chemical analysis via x-ray photoelectron spectroscopy confirmed that films individually deposited at oxygen levels of 50% and 60% are mixed-valent, consisting largely of ReO<sub>3</sub> (Re<sup>6+</sup>), with contributions from ReO<sub>2</sub> (Re<sup>4+</sup>) and Re<sub>2</sub>O<sub>7</sub> (Re<sup>7+</sup>). Note that films deposited at 50% oxygen content also contained up to 15% Re<sub>2</sub>O<sub>3</sub> (Re<sup>3+</sup>). Further monitoring of the films' valence states, after an environmental exposure time of 30 days, indicates a correlation between structural instability and the presence of both Re<sub>2</sub>O<sub>3</sub> and Re<sub>2</sub>O<sub>7</sub>. Analyses via XPS and *ex situ* spectroscopic ellipsometry indicate that films deposited within an atmosphere of 60% oxygen do not contain Re<sup>3+</sup> and demonstrate stable surface chemistry and optical behavior throughout the 30 day period, while those deposited at 50% oxygen experience significant degradation. Increasing the stability of mixed-valent Re-O films could give rise to more widespread use of rhenium in optics and catalysis, especially in applications where mild moisture exposure is unavoidable.

12:00pm **AS-ThM13 Multi-Technique Surface Analysis of Geological Samples, Including sub-10 Micron Spectroscopic XPS Imaging**, Paul Mack, Thermo Fisher Scientific, UK

A single geological sample may have multiple phases, each with different chemical bonding environments. Geologists will typically have access to SEM-EDS, giving them elemental information from the different grains (from bulk depths). When it comes to chemical information, however, XPS provides a unique ability to easily acquire data from these small grains. It offers quantitative chemical bonding data with a probe size small enough to acquire data from individual phases.

In this work, rock cross-sections were analysed with XPS to quantify the elements in different phases and to identify and quantify the oxidation states of elements in these regions. The analysis can be divided into four main sections: 1) Finding the features of interest, 2) Aligning the X-ray spot on the features, 3) Acquiring the XPS data and 4) Processing the XPS data to answer the key questions about chemical bonding states.

Any XPS tool used for this analysis needs to have a high quality optical system, enabling to geologist to rapidly find the features of interest, with a live optical feedback system. The grains were typically 10s of microns in size, so a small X-ray analysis area is required. This small area analysis was achieved in two different ways: shrinking the

X-ray spot to match the feature size or collecting spectroscopic parallel imaging data. In the latter case, every pixel in the image has full XPS data allowing the analyst to perform sub-10mm area analysis directly from the X-ray image.

Techniques complementary to XPS can also help provide a more complete characterization of geological samples. SEM/Auger can offer analysis with a much smaller probe size than XPS, but it is necessary to charge compensate during the experiment. Charge compensation methodology will be discussed in this work.

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