Wednesday Afternoon, October 30, 2013

Atom Probe Tomography Focus Topic
Room: 203 A - Session AP+AS+MI+NS+SS-WeA

APT and FIM Analysis of Catalysts and Nanoscale Materials

Moderator: P.A.J. Bagot, Oxford University, UK

2:00pm **AP+AS+MI+NS+SS-WeA1 Atom Probe Tomography Characterization of Engineered Oxide Multilayered Structures**, ***S.A. Thevuthasan***, *M.I. Nandasiri, A. Devaraj, D.E. Perea, T. Varga, V. Shutthanandan*, Pacific Northwest National Laboratory

There has been growing interest in developing materials which possess high oxygen ionic conduction at low temperatures for solid oxide fuel cell applications. In our group, we have been developing trivalent element doped creia/zirconia multilayer thin film structures for this purpose. We have grown (i) multilayers of high quality samaria doped ceria (SDC) and scandia stabilized zirconia (ScSZ) films, and (ii) samaria and gadolinia co-doped high quality ceria films using oxygen plasma-assisted molecular beam epitaxy (OPA-MBE). These films exhibit significantly higher oxygen ionic conduction at intermediate temperatures in comparison to bulk materials. Although we have demonstrated that these structures possess high oxygen ionic conduction at low and intermediate temperatures, we haven't established the mechanisms associated with the enhancement in oxygen ionic conduction through these engineered heterogeneous interfaces.

Atom Probe Tomography (APT) can provide quantitative three-dimensional chemical analysis of materials with lateral and depth resolutions in the order of 0.2-0.3 nm and chemical sensitivity up to parts-per-million levels with field-of-view on the order of $100 \times 100 \times 100$ nm^3. Although APT has been extensively used to characterize metals, it is in its infancy in characterizing oxides and insulators. In addition, multilayer structure adds additional complications to the characterization of the doped ceria/zirconia multilayers. In this study, we have synthesized high quality SDC and ScSZ multilayers and used surface impedance spectroscopy to carry out detailed analysis of oxygen ionic conductivity as a function of individual layer thickness and dopant concentration. As a part of this study we attempted coupled scanning transmission electron microscopy and atom probe tomography to study the oxygen vacancy and dopant distributions along with the inter-diffusion and dopant segregation at the interfaces. These STEM/APT findings are correlated to the conductivity measurements and these results will be discussed.

2:20pm **AP+AS+MI+NS+SS-WeA2 Correlative Atom Probe Tomography and Transmission Electron Microscopy of Metal-Dielectric Composites**, ***A. Devaraj***, *R.J. Colby, D.E. Perea, S.A. Thevuthasan*, Pacific Northwest National Laboratory **INVITED**

Metal-dielectric composite materials are ubiquitous in several important engineering applications ranging from catalysis to semiconductor devices. The technological advances in such fields heavily depend upon the development of three-dimensional characterization capabilities that can accurately identify composition and structure at sub-nanometer spatial resolution and ppm-level composition sensitivity. Atom probe tomography (APT) has already demonstrated its potential in three-dimensional characterization of bulk metals and alloys, however the theoretical understanding of the evaporation behavior of dielectrics and metal-dielectric composites, as well as possible artifacts during laser assisted APT, is still at its infancy. 3D transmission electron microscopy (TEM) tomography on the other hand is currently restricted by long acquisition times and reconstruction artifacts. A correlative TEM-APT approach can help in extending the applicability of APT analysis and TEM beyond the current boundaries by providing not only complementary information but also a deeper understanding of the possible artifacts. This presentation will focus on such a correlated TEM-APT approach to investigate the field evaporation behavior of metal dielectric composites with metallic nanoparticles embedded inside oxides as well as planar structures with metallic thin films on single crystalline oxide substrates. Aberration-corrected TEM high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) were used to image the APT samples before and after APT analysis. STEM imaging after interrupted APT analysis was used to capture snapshots of evolving tip shape. Such understanding, when combined with novel APT reconstruction processing, can greatly aid in expanding the capabilities of APT analysis to novel complex heterogeneous metal-dielectric composite materials.

3:00pm **AP+AS+MI+NS+SS-WeA4 High Temperature *In Situ* Diffusion Studies of Gas – Solid Reactions with Atom Probe Tomography**, ***S. Dumpala***, *S.R. Broderick*, Iowa State University, *P.A.J. Bagot*, University of Oxford, UK, *K. Rajan*, Iowa State University

The diffusion couples of in-situ metal-oxygen reactions are analyzed through laser pulsed atom probe tomography (APT) reactions and experiments. Using ternary metal compounds, the relative diffusion and segregation of the different species with oxidation is assessed. This provides a further level of information beyond typical diffusion profiles by considering relative changes in metallic species, providing basic material descriptions at a higher resolution then ever previously measured.

The oxidation experiments were performed in-situ and at temperatures of ~450 ^{O}C and at 10^{-3} torr pressures. Given atom probe's atomic scale spatial resolution, chemical diffusion over a nanometers wide range across the chemical interface is assessed with exceptional accuracy, and the identification of compound formation is quantified. By performing all reactions within an in-situ APT reaction cell along with initial (in-situ) cleaning of the samples, any effects due to native oxidation or contamination are eliminated, which is particularly important when considering atomic scale spatial resolution and femto-scale chemical resolution. The challenges associated with performing in-situ reactions and the potential of this new experimental set-up to study a far wider range of treatment conditions, particularly when coupled with a laser-pulsed APT are discussed.

3D results of binary and ternary catalytic alloys are presented and the advancements in studying catalytic reactions are discussed. Aluminum and silicon samples were also oxidized and chemically-mapped atomic scale imaging of the material were processed to identify the preferred stoichiometry of aluminum oxides as a function of the distance from the aluminum-oxygen interface. This demonstrated ability of the APT to simultaneously image and chemically quantify gas-metal interactions at the atomic level enables us to systematically quantify these interactions as a function of material chemistries, crystallographic orientations and important microstructural features.

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4:00pm **AP+AS+MI+NS+SS-WeA7 Atomic Scale Characterisation of Catalyst Material**, ***T. Li***, *P.A.J. Bagot, S.C.E. Tsang, G.D.W. Smith*, Oxford University, UK **INVITED**

Bimetallic heterogeneous catalysts have proven remarkably successful in catalysing a wide range of important processes, in fuel-cells, exhaust emission control and in hydrocarbon processing. However, the effects of the operating environment on the surface composition, structure and stability of the noble metal catalysts are poorly understood at the atomic-scale. This knowledge will be required to produce the improved catalysts needed for future energy- and materials-efficient technologies.

Atom probe tomography offers a unique method for studying these materials, offering atomic-scale chemical identities of the catalyst surfaces and chemisorbed species. We have used APT to show a rich variety of behaviour in Pt-based alloys, investigating the effects of high temperature/pressure oxidation. These reveal pronounced surface segregation behaviour, strongly dependent on the treatment conditions, crystallographic plane and alloy composition. Furthermore, while subsequent reduction treatments remove formed oxides, the marked changes to the metallic surface compositions remain. Such results suggest using sequential oxidation and reduction treatments as an alternative synthesis method for designing and preparing nano catalysts with controlled surface compositions.

Another aspect of our work focuses on the investigation of the use of APT for characterizing catalyst nanoparticles either in colloidal dispersions or on the carbon supports. It is very challenging to fully characterize these complex 3D architectures by conventional electron microscope technique. In this work, we have for the first time demonstrated the use of APT for the analysis and characterization of such materials in atomic detail. Alongside a description of the preparations, we will also present a range of results from these catalysts materials, highlighting the correction between catalytic efficiency and the atomic-scale chemical/structural information uniquely provided by APT.

4:40pm **AP+AS+MI+NS+SS-WeA9 From Field Ion Microscopy of Tips to 3D Atom Probe Tomography of Real Catalyst Nanoparticles**, ***N. Kruse***, Université Libre de Bruxelles, Belgium **INVITED**

This contribution will address some major achievements made in the application of Field Ion Microscopy (FIM) and 1D/3D Atom-Probe (AP) techniques to study catalysis-related problems. In particular, we shall demonstrate the unique capabilities of FIM to image reaction-induced morphological reshaping of single metal nanoparticles conditioned in the form of tips. As an example, we show how a nearly hemispherical Rh nanoparticle is transformed into a polyhedral morphology in the presence of oxygen gas.

In a second example, we shall inspect the use of 1D AP as a tool to provide a detailed kinetic analysis of adsorption/thermal desorption processes. As an example, measurements of the mean life time of NO molecules adsorbing on ~ 60 atomic sites of a (111) Pt facet will be presented. A quantitative evaluation of the data in terms of activation energies for desorption along with pre-exponential factors becomes possible by temperature variation.

Third, we shall consider the combined approach of FIM and 1D AP in imaging the dynamics of surface reaction processes while mapping the local chemistry during these processes. As an example, we shall present results of the catalytic reaction between oxygen and hydrogen on the surface of a Rh nanoparticle. Moving reaction fronts are followed here by using video techniques. The observed patterns demonstrate a strong non-linearity merging into oscillating reaction behavior between oxygen and hydrogen. 1D atom-probe measurements during oscillations allow distinguishing between oxygen- and hydrogen-covered surface patches. They also indicate the participation of sub-surface oxygen species in a feedback process. The oscillatory behavior has been successfully modeled using theoretical models of non-linear processes along with DFT.

Finally, we show that 3D AP can also be used for a chemical mapping of single nanosized grains of real catalysts. Using focused ion beam techniques, "CoCuMn" real catalyst particles as used for the selective production of 1-alcohols from synthesis gas (CO/H_2), can be conditioned in the form of tips. A 3D AP analysis of a single catalyst grain demonstrated the occurrence of a core-shell structure with Co forming the core. Interestingly, all three metals are found to be present in a 2nm thick shell which is otherwise dominated by large amounts of Cu. Such information is most important when it comes to establish relationships between catalytic activity/selectivity and surface chemical composition.

5:20pm **AP+AS+MI+NS+SS-WeA11 NO_2 Reduction over Pt and Rh Single Nanoparticles: Imaging with Nanometric Lateral Resolution**, ***C. Barroo****, *S. Lambeets, Y. De Decker, F. Devred, T. Visart de Bocarmé, N. Kruse*, Université Libre de Bruxelles, Belgium

Nitric oxides (NO_x) emissions from vehicles are harmful to human beings and may cause severe health issues. NO_x abatement is therefore highly desirable, but the development of viable solutions still represents a major challenge for catalyst makers, especially in the case of lean-driven vehicles. NO is known to be oxidized to NO_2 under lean-burn conditions in automotive engines, and subsequently reduced into N_2 during the rich-burn regime. In this work, we have investigated the catalytic reduction of NO_2 over platinum and rhodium field emitter tips by means of Field Emission Microscopy (FEM). Real-time FEM is a powerful method for studying the dynamics of catalytic reactions that take place on the surface of the top of a nanosized metal tip, which acts as a catalytic particle. These studies are performed during the ongoing catalytic reaction which can be imaged in real time and space. Nanoscale resolution is achieved, providing a local indication of the instantaneous surface composition. Reaction-induced structural changes of the catalyst's surface can also be assessed with step-site resolution. FEM is based on the emission of electrons from the sample which can be affected by the presence of various adsorbates. Local variations of the work function are reflected in the form of a brightness pattern and the surface composition of the sample can be qualitatively investigated during the ongoing catalytic process, allowing for the determination of the elementary processes involved.

The microscope is run as an open nanoreactor, through a constant supply of gaseous reactants and constant gas-phase pumping of the reaction chamber, ensuring that the system is kept far from thermodynamic equilibrium. This may lead to non-linear dynamics. Among others, oscillating phenomena observed during the NO_2 reduction by H_2 over both Pt and Rh nanocrystal (whose diameter is ≈40 nm) are presented.

Data have been characterized by Fourier transforms, temporal autocorrelations and dynamical attractors that demonstrate the existence and robustness of the kinetic oscillations. Furthermore, the optimal parameters obtained for the reconstruction of the dynamical attractor from the experimental time series, give important information that can lead to a better understanding of the mechanism of the catalytic reduction of NO_2 over PGM nanoparticles.

5:40pm **AP+AS+MI+NS+SS-WeA12 Quantitative Three-Dimensional Compositional Analysis of Geologic Minerals using Atom-Probe Tomography**, ***J. Liu***, *D.E. Perea, R.J. Colby, B. Arey, O. Qafoku, A. Felmy*, Pacific Northwest National Laboratory

Carbon capture and sequestration within deep geological formations has become one of the most important options to mitigate the ever-growing environmental CO_2 emissions. The olivine group of minerals, X_2SiO_4 where X = Mg or Fe, hold promise as potential media to sequester carbon. Upon reaction of supercritical CO_2 (sc-CO_2) with fayalite (Fe_2SiO_4) or forsterite (Mg_2SiO_4), various oxide and carbonate phases result accompanied by a complex change in surface morphology. A combination of atom probe tomography (APT) and scanning transmission electron microscopy (STEM) is being used to map the complex composition across various site-specific interfaces in order to better understand the complex phases that form upon reaction with sc-CO_2. The advantage of APT analysis is that it can provide a unique 3-D atomic-scale compositional map with a part-per-million sensitivity to allow tomographic mapping of low-level impurities such as Li. Optimization of the APT analysis conditions will be discussed leading to the optimal stoichiometric composition. The results demonstrate the viability of using APT analysis to study the composition geological minerals for energy and environmental applications.

*** NSTD Student Award Finalist**

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