Chemical Analysis and Imaging at Interfaces
Room Ballroom BC - Session CA-ThP

Chemical Analysis and Imaging at Interfaces Poster Session

CA-ThP-1 Depth Profiling of Perovskite Tandem Solar Cells Using Small Ar Gcib in Cluster Sims at Cryogenic Temperatures, *Kate McHardy, Naoko Sano,* ***Mark Mills,*** Ionoptika Ltd., UK

Many Secondary Ion Mass Spectrometry (SIMS) instumentscan perform at cryogenic temperatures, however, complex sample handling requirements and high cryogen consumption have meant that such experiments have hitherto been expensive and complicated. Utilising Ionoptika's J Series III cluster SIMS instrument with Cryo stage, we show that long-term Cryogenic studies may be carried out on both soft and hard materials, with demonstrable improvements in results compared to RT analysis. We demonstrate 3D depth profiling of perovskite solar cells and show that the precision of the depth profile is increased at Cryo temperatures when compared with RT analysis. The current common approach to analyse such samples is to peel off the hardest capping layer and then analyse the perovskite layers using Ar GCIB to sputter and Bi to analyse. Alternatively, a Cs beam may be used to sputter to just above the interface, and then low energy an Ar GCIB and Bi beam used for sputtering and analysis. However these approaches are flawed; the peeling process can cause migration of elements to the free surface, and Cs and monoatomic Ar sputtering can cause intermixing of consecutive layers.The J Series III Cluster SIMS system employs GCIB as the primary ion beam which can sputter and analyse simultaneously, meaning no sputter-only cycles. For thin layers, this is crucial, asit precludes loss of information about the layers and/or interface. In addition, the GCIB used has a high (70 kV) beam energy and provides a range of cluster sizes from monoatomic to large cluster sizes such as 30k. We have previously demonstrated use ofsmaller cluster beams to sputter though 1.5 um thickness of perovskite solar cell samples from the capping layer to the glass substrate with less preferential sputtering and intermixing effects. Therefore, J Series III analysis using a small cluster GCIB promises to show more 'genuine' information than the current dual beam method for hard and mixed materials including metals and organics.In this work, pristine and aged samples of perovskite tandem solar cells are analysed with an Ar350 Cluster at 70 keV beam in the J Series III at RT and cryo temperatures to demonstrate the suitability, less intermixing effect and lack of preferential sputtering especially at cryo temperatures that show higher depth resolution and sputter rate with less damage.We conclude that analysis of hybrid semiconductor samples results in superior data when conducted with small clusters at Cryogenic temperatures.

CA-ThP-2 Uncovering Coke-Resistant Two-Dimensional Metal Carbide Catalysts Using ToF-SIMS, ***Tobias Misicko,*** Louisiana Tech University and Oak Ridge National Laboratory*; Gabriel Parker,* Oak Ridge National Laboratory*; Yang Xiao,* Louisiana Tech University*; Xiao-Ying Yu,* Oak Ridge National Laboratory

Catalysts can be described by three important aspects activity, selectivity, and stability. Activity is the ability of a catalyst to convert reactants into products. Selectivity is the ratio of the desired product to the total amount of converted molecules. Stability is the ability of a catalyst to maintain activity with respect to time on stream (TOS, time since initial contact of reactant gas to the catalyst bed) in continuous reactors. MXene, a class of two-dimensional metal carbides, can be used as a support material to create a coke-resistant nanolayer catalyst with excellent activity, selectivity, and stability. MXene has empirical formula of $M_{n+1}X_nT_x$, where M is an early transition metal, X is a carbon or nitrogen, and T is a surface functional group (such as F^- or OH^-). In our prior studies,[1,2] platinum (Pt) was loaded onto Mo_2TiC_2 MXene using incipient wetness impregnation to synthesize a 0.5% (wt.) Pt/Mo_2TiC_2 Pt nanolayer MXene catalyst. The Pt nanolayer catalyst exhibited excellent activity with turnover frequencies (TOFs, converted molecules per surface Pt atom) of 0.4~1.2 s^{-1} for converting methane[1] and ethane[2]. 0.5% Pt/Mo_2TiC_2 displayed high selectivity, with over 98% to C_2 products for non-oxidative coupling of methane (NOCM) and over 95% selectivity for catalytic dehydrogenation of ethane to ethylene. Robust catalyst stability is obtained with no loss in catalytic activity for 72 hr. and 24 hr. for NOCM and ethane dehydrogenation, respectively, owing to its strong coke-resistance. However, the active site and surface activity are not easy to study. In this presentation, we used time-of-flight secondary ion mass spectrometry (ToF-SIMS) to investigate MXene catalytic effects. ToF-SIMS is a highly sensitive surface analysis technique, capable of molecular, atomic, and isotopic analysis. Depth profiling and mass spectral mapping allow for analysis of subsequent monolayers of the catalyst's surface. Measurements, including surface spectra, two-dimensional imaging, secondary electron imaging, and depth profiling (three-dimensional imaging), were used to probe the surface and reveal structures of both unloaded Mo_2TiC_2 MXene support and 0.5% Pt/Mo_2TiC_2 nanolayer MXene catalysts. The large dispersion of Pt^+ ions throughout the bulk of Pt/Mo_2TiC_2 nanolayer MXene supports the hypothesis that the MXene channel prohibits access to the terrace site, a critical site for the structure-sensitive coking reaction.

[1] Li Z. *et al.*, *Nano Research,* 17 (**2024**) 1251–1258.

[2] Li Z. *et al.*, *Nature Catalysis,* 10 (**2021**) 882–891.

CA-ThP-4 Tapping into Charge Storage with Operando-XPS using Coplaner Capacitors and Ionic Liquid Mixetures, *Ezgi Kutbay,* ***Sefik Suzer,*** Bilkent University, Turkey

We use X-Ray Photoelectron Spectroscopy under bias to track surface population and electrical potentials on multilayered graphene electrodes with two ionic liquid mixtures, one containing the same cation (DEME+) and two different anions (TFSI- and BF4-) and the other one with two different cations (DEME+ and Rb+) and same anion (TFSI-). As bias increases, peak intensities change and binding energies shift, revealing both ion concentrations and also the local electrical potentials simultaneously. In addition the capacitance of the device increases significantly, providing crucial insights for developing new energy storage devices.

CA-ThP-6 Meeting the Demand for Surface Sensitivity: The Role of LEIS, ***Joshua Pinder*** [1]*,* Brigham Young University*; Stanislav Prusa,* Central European Institute of Technology, Czechia*; Matthew Linford,* Brigham Young University

Low-Energy Ion Scattering (LEIS) provides unmatched sensitivity to the outermost atomic layers of materials, making it a critical tool for surface analysis. This poster presents a practical guide to LEIS spectral interpretation, featuring spectra from a diverse range of materials. While covering key theoretical aspects, the focus remains on practical insights for researchers who rely on LEIS data, whether through collaboration or literature. Topics include surface peak identification, reionization effects, multiple scattering, contamination impacts, and material-specific spectral features. Spectra from modern high-sensitivity LEIS instruments illustrate both fundamental and advanced phenomena across various materials of technological interest. By clarifying LEIS spectral characteristics and applications, this guide aims to enhance accessibility and understanding within the broader scientific community.

CA-ThP-7 Mass Spectral Molecular Mapping Shows Benefits of Thermal Evaporation in Prelithiated Silicon-Based Composite Electrodes, ***Ivan Matyushov***[2]*, Gabriel Parker, Amanda Musgrove, Gabriel Veith, Xiao-Ying Yu,* Oak Ridge National Laboratory

Key words: ToF-SIMS, prelithiation, anode, solid-state lithium-ion battery, lithium silicateSilicon carbon composites have become increasingly popular as potential anodes for solid-state lithium-ion batteries due to their large storage capacity. However, their current application is inhibited by the disruptive volume expansion and continuous solid electrolyte interface (SEI) layer formation that reduces their initial columbic efficiency (ICE). Prelithiation is used to counteract the loss of lithium ion (Li^+) by adding reserved lithium ions to the electrode. Prelithiation via thermal evaporation is a newly developed technique with limited studies on its effectiveness and process variations. Thermal evaporation was done through a 400-steel mesh placed over the electrode which directed the lithium metal deposition and diffusion into 'islands' or channels in a set of electrodes. Using this steel mesh resulted in less strain and volumetric expansion in the electrodes. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is used to highlight the benefits of prelithiation via thermal evaporation with a steel mesh in this study. Three ToF-SIMS measurement modes are used to visualize the deposition of lithium into 'islands', to identify Li_xSi_y alloy and $Li_xSi_yO_z$ silicate formation, and to display the distribution of lithium throughout the electrodes. The SIMS molecular imaging results validate the formation of the LiSi alloy and $Li_xSi_yO_z$ silicate upon prelithiation. Through depth profiling three-dimensional and surface two-dimensional imaging in SIMS, we confirm that prelithiation by thermal evaporation effectively incorporates lithium into the silicon composite anode as desired. The

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[1] **JVST Highlighted Poster**

[2] **JVST Highlighted Poster**

multimodal mass spectral imaging results help validate the effectiveness of thermal evaporation for prelithiation, particularly in combination with a steel mesh.

CA-ThP-9 Evaluation of Imbedded Barium in Graphite for Nuclear Engineering in ToF-SIMS*, **Gabriel Parker**, Thomas Muth, Victor Bautista, Xiao-Ying Yu,* Oak Ridge National Laboratory, USA

Advanced manufacturing of cermets, heat-resistant materials made of ceramic and sintered metal, is necessary for radio isotope production to decrease waste and increase efficiency. The High Flux Isotope Reactor (HFIR) at the Oak Ridge National Laboratory currently uses Al as the filler material for irradiation targets. While Al has offered the ease of use and high thermal conductivity, it is limited by the post processing procedures creating a high charge density of the Al cation, creating instable aluminum nitrates, and forming oxidation decreasing the overall performance of the irradiation target. Transitioning from Al to a graphite matrix could reduce the issues aluminum poses. Graphite has similar thermal stability, thermal conductivity, and chemical properties. The manufacturing process using carbon can reduce waste by lowering solution volumes and overall complexity. ^{223}Ra is a radio isotope used for cancer treatments and is produced via a series of beta decays starting with ^{226}Ra. To test method development, Ba, is used as a surrogate to radium. This work examines the barium encapsulation by graphite using time-of-flight secondary ion mass spectrometry (ToF-SIMS). Specifically, high resolution spectroscopy and 2D/3D imaging modes were used to study the $BaCO_3$ pellets prepared in different manner.Current manufacturing process uses a mixture of graphite and barium carbonate either vacuum hot pressed or cold pressed and sintered. The mass spectrometry results verify that BaC as this is the preferred extraction radio isotope and not the oxide or carbonate. Also, depth profiling results show the $BaCO_3$, BaC_2, and BaO distributions across the surface and into the bulk of the pellet, indicative of the usefulness of different pellet processing steps.

Key words:

Barium, Radium, Graphite, Advanced Manufacturing, Nuclear Engineering, Radioisotopes, ToF-SIMS

CA-ThP-10 Potential Use of REELS and Electron Elastic Peak Spectroscopy for Measuring and Mapping Atomic Mass resolved distributions in SEM*, **Philippe Staib**,* WSI

Elastically backscattered electrons suffer a small kinetic energy loss with the interacting atom. The interaction is electrostatic and is described as a Rutherford backscattering process. Energy Shifts of the peak caused by the recoil energy loss only depends on the atomic mass M of the surface atom. The broadening and splitting of the elastic peak is described in [1]. The recoil energy loss is given by the simplified formula:

$E_{recoil} = 4 (m_e / M) \sin^2 (\theta/2)\ Ep$

with M the mass of the recoil atom, m_e the electron mass, θ the scattering angle and Ep the electron kinetic energy in eV.

The measurement of the recoil energy loss requires a high energy resolution analyzer to accurately measure the elastic peak position and shape. The compact energy analyzer described in [2,3,5] is mounted in a SEM chamber. The intensity of the elastic peak is strong and allows the measurement of recoil losses at low primary beam current bellow one nA thus well compatible with SEM beam currents. The elastic peak intensity depends upon the backscattering cross-section and atomic density. The backscattering coefficient can be given by the empirical Everhart formula based on the Rutherford model [4]. It essentially depends upon the atomic number Z.

Therefor the elastic peak shows an energy shift related to the atomic mass M of the scattering atom and an intensity corresponding to the Z and atomic density of the scattering atom. At 10 keV primary beam energy the calculated recoil loss values are:

Ag (108) 0.1 eV, C (12) 0.91 eV, O (16) 0.7 eV, H (1) 10 eV

The present analyzer can detect energy shifts of low mass materials from H to Si.

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CA-ThP-11 Edge-Localized Strain in MoS_2 Nanobubbles Resolved at 5 nm by Chemical Imaging and Geometric Mechanics*, **Sayantan Mahapatra**,* Argonne National Laboratory, USA*; Soumyajit Rajak, Nan Jiang,* University of Illinois - Chicago*; Jeffrey Guest,* Argonne National Laboratory, USA

The formation of nanoscale bubbles is an unavoidable consequence during the transfer of two-dimensional materials onto target substrates, driven by van der Waals interactions at the interface. While often viewed as imperfections, these nanoscale bubbles have garnered considerable scientific interest due to the substantial in-plane strain gradients they induce, which in turn give rise to a variety of intriguing optoelectronic effects, particularly in semiconducting transition metal dichalcogenides. Determining and analyzing the strain distribution within nanobubbles at the nanoscale is crucial for advancing our understanding of these underlying strain-induced effects. Here, we present a high-resolution scanning tunneling microscopy-based tip-enhanced Raman spectroscopic investigation of localized nanoscale strain distribution within the nanobubbles formed between the monolayer MoS_2 and Au interface. By employing cryogenic temperature (78 K), we successfully differentiate the nanoscale Raman signatures between the nanobubble edge and pristine MoS_2. We verify a maximum tensile strain of ∽1.15–1.34% at the nanobubble edge, which gradually diminishes toward the center, yielding a cross-sectional strain profile consistent with a doughnut-shaped distribution. Furthermore, we report achieving ∽5 nm spatial resolution in probing such edge-localized strain within the nanobubble. In addition, comparative average strain analysis of such MoS_2 nanobubbles is conducted via geometric mechanistic analysis, such as membrane and nonlinear plate theories, providing key insight into the geometric nature near the bubble edge. Our findings provide fundamental information about strain-induced nanoscale chemical understanding of 2D materials on the nanometer scale, paving the way for practical applications of nanobubbles in strain-engineered optoelectronic devices.

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