In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Focus Topic
Room Hall D - Session IS-ThP

In-Situ and Operando Spectroscopy and Microscopy for Catalysts, Surfaces, & Materials Poster Session

IS-ThP3 Challenges and Current Progress in Characterizing the Solid Electrolyte Interface in Lithium-Sulfur Batteries*, **Manjula Nandasiri**, A.M. Schwarz, V. Shutthanandan,* Pacific Northwest National Laboratory*; P. Kandasamy,* Pusan National University, Republic of Korea*; S.A. Thevuthasan,* Qatar Environment and Energy Research Institute*; V. Murugesan,* Pacific Northwest National Laboratory

Lithium-sulfur (Li-S) battery is a promising candidate to replace Li-ion battery due to their high theoretical specific capacity and energy density. However, there are some challenges to overcome to realize the practical applications of Li-S batteries. One of the most critical challenges to overcome is the shuttling of long chain lithium polysulfides (LiPS), which results in the formation of solid-electrolyte interface (SEI) layer on the electrodes and fading of the battery capacity. The constituents and properties of the SEI layers are dependent on the electrolyte and not very well-understood. It was suggested that the application of *in-situ* or *in-operando* techniques can capture the dynamic changes in the SEI layer during the battery cycling. Thus, our aim was to study the fundamental properties of SEI layer of various electrode-electrolyte systems in their working environment using *in-situ* XPS and imaging XPS. In order to do that, we developed an in-situ XPS capability at Environmental Molecular Sciences Laboratory located in Pacific Northwest National Laboratory.

Analyzing the SEI layers *in-situ* using XPS techniques is very challenging task due to the nature of the electrolytes and their behavior in vacuum systems. Therefore, a vacuum friendly ionic liquid (1-butyl-1-methylpyrrolidinium bis(trifluoromethyl-sulfonyl)imide) was selected as the electrolyte along with Li and graphite electrodes for the in-situ XPS characterization of SEI layers. Using this *in-situ* configuration, we were able to determine the composition of SEI layers formed on Li anode and graphite cathode in Li/ionic liquid/graphite battery system. These XPS results show the gradual formation of LiPS compounds and the decomposition of electrolyte on Li anode with the formation of LiF during the charging and discharging process.Moreover, the elemental and chemical state distributions of SEI layer were mapped using *in-situ* imaging XPS. In addition, we continued the SEI layer characterization of electrodes cycled in the electrolytes which cannot be handled in vacuum using a glove box attached to the XPS system. The XPS and imaging XPS results of these studies will be extensively discussed.

IS-ThP4 Traceable Calibration of High-Quality Pitch Standards Based on an Atomic Force Microscopy System Combined with a Piezo-Actuated Flexure Stage*, **Chien-ying Su**, N.N. Chu, M.H. Shiao, C.N. Hsiao, F.Z. Chen, J.A. Yeh,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, Republic of China

A high-precision atomic force microscope (AFM) metrology system has been established for traceable calibration of transfer standards based on a commercial AFM system and a piezo-actuated flexure stage. By adopting a DSP-based controller, this system is capable of providing high-level nanomotion control. The piezo-actuated flexure stage includes capacitive position sensors in all three axes for highly linear motions over 110 mm scan size and as low as one nanomenter out-of-plane motion. And the capability of subnanometer resolution with linearity error as less as 0.05% is achievable. For measuring periodical structures such as pitch standards, two operation modes are applicable: (a) Combined scanning mode, where the position of the closed-loop displacement stage is controlled point by point while the AFM scanner head measures and records the height variations simultaneously; (b) Direct scanning mode, where the closed-loop displacement stage actuates three axes offsets which are multiples of the pitch length according to the feedback signal of the AFM scanner head in order to locate edge profiles.

In addition, inductively coupled plasma reactive ion etching (ICP-RIE) process has been applied for high-quality pitch standard fabrication. System details, characteristics and results for pitch standard calibrations are presented. System calibrations through transfer standards such as 99.999 nm pitch standard with expanded uncertainties of 0.014 nm establish traceability to the national metrology institute Physikalisch-Technische Bundesanstalt (PTB). The estimated combined uncertainties of this system for pitch standard calibration are in accordance with the Guide to the Expression of Uncertainty in Measurement (ISO GUM).

Keywords: high-precision, transfer standards, nanomotion, flexure stage, feedback, ICP-RIE, combined uncertainties, metrology

IS-ThP5 XPS Enables Visualization of Charge Screening in Metal-ionic Liquid Interfaces with Temporal- and Lateral-resolution*, M.T. Camci,* Mrs, Turkey*; P. Aydogan, B. Ulgut, C. Kocabas, **Sefik Suzer**,* Bilkent University, Turkey

X-ray photoelectron spectroscopic (XPS) investigation of charge screening across two gold electrodes fabricated on a porous polymer surface which is impregnated with an ionic liquid (IL) will be presented. The IL provides a sheet of conducting layer to the insulating polymer film, and allows monitoring charging and screening dynamics at the polymer + IL / vacuum interface in a laterally resolved fashion across the electrodes. Time-resolved measurements are also implemented by recording F1s peak of the IL, while imposing 10 mHz square-wave-pulses (SQW) across the two electrodes in source-drain geometry. Variations in the F1s binding energy reflects directly the transient local electrical potential, and allow us visualize screening of the otherwise built-in local voltage drop on and across the metal electrodes in the range of millimeters. Accordingly, the device is partitioned into two oppositely polarized regions, each following polarization of one electrode through the IL medium. On the other extreme, upon imposing a relatively fast 1 kHz square-wave pulses the charge screening is prevented and the device is brought to assume a simple resistor role. The presented structure and variants of XPS measurements, enabling to record voltage transients in unexpectedly large lateral distances away from the interface(s), can impact on understanding of various electrochemical concepts.

IS-ThP6 Ambient Pressure Photoemission Instrumental Development and Applications within the Field of Energy Related Research*, **John Åhlund**,* Scienta Omicron, Sweden

Ambient pressure photoelectron spectroscopy (APPES) is a rapidly developing technique, suitable for studies in the field of energy harvesting, e.g. solar cells and energy storage, e.g. batteries. We have developed two analysers, capable of measuring samples with a surrounding gas pressure in the mbar range.

Here we present the design and performance of these two new hemispherical electron energy analyzers, the Scienta Omicron HiPP-2 analyser, designed for energies ranging from x-ray photoelectron spectroscopy (XPS) to hard x-ray photoelectron spectroscopy (HAXPES) and the Scienta Omicron HiPP-3 analyser, designed for XPS energies. Where the latter also having imaging capabilities.

For laboratories both analyzers can be equipped with an Al Kα X-ray anode, as demonstrated in Eriksson et al RSI 85(2014)075119 and Edwards et al, NIMA, 785(2015)191. Firstly the performance of the analysers in combination with Al Kα X-rays is demonstrated using standard test samples and procedures, including a demonstration of the HiPP-3 spatial performance under ambient pressure conditions. Secondly the performance is linked to a general discussion about sample to first aperture distance (Kahk et al, JEPEC, 205(2015)57).

Finally we will demonstrate the performance of the HiPP-2 analyzer with applications examples from a dye-sensitized solar cell interacting with water (Eriksson et al Top. Cal. 59(2016)583) and a method to study the battery solid/liquid interface. For the first time the presence of a liquid electrolyte was realized during photoemission measurements (Maibach et al RSI 86(2015)044101).

IS-ThP7 Highly Sensitive Ion Trap Mass Spectrometer for Inline Process Control*, G. Fedosenko, H.-Y. Chung, M. Aliman, A. Laue, R. Reuter, V. Derpmann, M. Antoni, L. Gorkhover, **Tina Graber**,* Carl Zeiss SMT GmbH, Germany

Real-time inline control of process gas compositions with high sensitivity has been of particular importance in recent years in the semiconductor industry and beyond. Most of the real-time process gas analysis was carried out with differentially pumped Residual Gas Analyzer (RGA) which are based on a linear quadrupole mass filtering technique. To generate a complete mass spectrum, a RGA usually needs a few minutes which is often too slow for real-time inline process control. A new process control mass spectrometer, based on Fourier-Transform 3D-Quadrupole Ion Trap technology, is more appropriate for real-time inline process and will be presented in this work.

The 3D-Quadrupole Ion Trap mass spectrometer (*iTrap®*) by ZEISS is installed in a vacuum chamber (120mm x 120mm x ~ 500mm) with an ALD valve for pulsed gas sample injection (pulse duration ~ 50ms). An electron gun is used for ionization of the gas pules. The Ion Trap achieves ion trapping and accumulation by means of a radio frequency applied to the ring electrode of the trap. With the aid of advanced electronic amplifiers and selective ion excitation technique the ion oscillations can be measured electrically without using any separate particle detector. The mass spectrum is finally obtained by a Fourier Transform of the recorded electrode current signal in less than one second.

Real-time measurements of the hydrogen plasma cleaning process of Sn contaminated samples were performed with the *iTrap®* mass spectrometer. The working pressure of the plasma cleaning process was 0.5 mbar. Decreasing signal of SnH4 and other contaminations from the samples which are directly correlated to the cleaning process were observed with *iTrap®*. This result is extremely useful for the process control of Plasma processes and inline real-time contaminations control for high-end applications such as the EUV Lithography manufacturing.

MOCVD process for GaN growth was also investigated with *iTrap®*. The result shows that gas species related to wafer holder contamination, gas phase reaction products and dopant memory effects due to Cp2Mg could be observed clearly. These information will help the user to recognize process drift and/or minimize chamber cleaning intervals.

The new mass spectrometer of ZEISS (*iTrap®*) has successfully detected real-time SnH4 signal in the hydrogen plasma cleaning process. Inline measurement at a MOCVD chamber showed that *iTrap®* is capable to detect reaction products, contaminations on the wafer holder and dopant memory in real-time. These results demonstrate that *iTrap®* is a very sensitive and fast process mass spectrometer suitable for real-time inline process monitoring.

IS-ThP8 Real-time State-resolved Reactivity Measurements as a Probe of Carbon Dissolution Kinetics on Ni(111)*, Eric Dombrowski, E.H. High, A.L. Utz,* Tufts University

The steam reforming of methane to produce hydrogen occurs on an industrial scale at catalyst temperatures exceeding 1000 K, but most of the published sticking data on the methane / nickel system focuses on low surface coverages and surface temperatures, T_s, below 650K. At higher T_s, the carbon products of methane dissociation dissolve into the nickel bulk, which prevents post-dose measurements of reactivity.

To address this limitation, we couple King & Wells molecular beam reflectivity measurements with modulated infrared laser excitation to quantify methane's dissociative chemisorption probability, S,over a wide range of incident fluxes and T_s. This new method simultaneously measures ground state and eigenstate resolved reactivities in real time. Each dose produces upwards of 20 independent reactivity measurements, increasing our precision greatly. Our ability to quantify S in real time reveals the coverage-dependent reaction probability, $S(q,T_s)$. Measuring the full adsorption isotherm further constrains our measured value of the initial sticking probability, S_0.

We measure $S(\Theta,T_s)$ for methane on Ni(111) over a wide range of T_s (500 - 1000 K) and reactive flux (from 0.004 to 0.40 ML/s). Under these conditions, methane initially dissociates into H and methyl fragments. The surface-bound methyls then dehydrogenate to C + 3H, and recombinative desorption of H at these surface temperatures is prompt. Initial measurements of $S(\Theta=0, T_s)$ show how elevated surface temperatures promote methane dissociation. As the dose proceeds, we observe coverage-dependent changes in $S(\Theta,T_s)$ that arise from the accumulation of C on and beneath the surface. These effects reveal the kinetics of carbon dissolution into bulk nickel starting with the initial CH bond cleavage event. We observe a sharp transition for the onset of observed site blocking. At all investigated reactive fluxes no site blocking occurs above T_s = 900 K. Below 900K, we observed a reactive flux dependent induction period as the carbon dissolution kinetics approach steady state. Observing how these kinetics change with reactive flux shows how the presence of surface and subsurface C can enhance or inhibit methane activation under the high temperature conditions present in a steam reforming reactor.

IS-ThP9 Design and Performance of Large Surface Area Graphene Liquid Cell for in Situ Electron Spectroscopy and Microscopy*, Hongxuan Guo,* National Institute of Standards and Technology (NIST)*; A. Yulaev, A. Kolmakov,* National Institute of Standards and Technology

For applications such as electrochemistry, environmental science or (photo-) catalysis it is important to characterize materials and interfaces in reactive liquid or aquatic environments. However, interface sensitive characterization techniques, such as X-ray photoelectron spectroscopy (XPS), XAS, Auger electron spectroscopy (AES), SEM, electron microscopies require high or ultrahigh vacuum environments for their operation. To circumvent these pressure gap challenges, the graphene membrane based environmental cells have been recently developed [1, 2, 3] Graphene is the strongest materials with one molecularly impermeable atomic layer thick and it is transparent to electrons and x-rays in a wide energy range. Therefore, it is the best separating membrane material so far for fabrication of liquid cell for the*in-situ* studies of liquid samples in high or ultra-high vacuum environments.

We report on high yield fabrication of double layer graphene capped multichannel matrix which can be impregnated with a large variety of liquids and electrolytes for in-situ SEM, EDS, SAM, XPS. The liquid life time inside a cell can reach many hours and is limited by the defects density in the graphene and interfacial diffusion between the graphene membrane and MCA matrix. Using SEM, in combination with EDS and XAS spectroscopies we analyzed the electronic structure and dynamics of water-graphene interface. Auger spectroscopy was used to analyzed the attenuation of the water generated Auger electrons by double layer graphene. Electrochemical graphene liquid cells have been fabricated via Pt electrodes atomic layer deposition deep in to the MCA matrix. , We performed first feasibility tests via electroplating and stripping of Cu on the surface of double layer graphene from $CuSO_4$ solution. This new sample platform provides a new experimental ground for characterization of liquid materials for energy, catalysis, biomedical and environmental research.

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Author Index

Bold page numbers indicate presenter