In Situ Spectroscopy and Microscopy Focus Topic
Room: 203 B - Session IS+AS+SS-ThM

Ambient Pressure XPS from Sophistication to Reality

Moderator: A. Thissen, SPECS Surface Nano Analysis GmbH

8:40am **IS+AS+SS-ThM3 Ambient Pressure XPS Observation of Electrode Surfaces during Electrochemical Reactions**, *H. Sanchez Casalongue, S. Kaya, D.J. Miller, D. Friebel, A. Nilsson,* ***H. Ogasawara***, SLAC National Accelerator Laboratory **INVITED**

The sluggish kinetics in oxygen reduction reaction (ORR) is one of key challenges in polymer electrolyte membrane fuel cells (PEMFCs). Understanding the ORR mechanism under operating conditions is essential to isolate parameters that allow for high PEMFC efficiencies. Through the use of ambient pressure photoemission spectroscopy (APXPS) at Stanford Synchrotron Radiation Lightsource (SSRL) [1], we identified the surface speciation of the fuel cell Pt cathode under different operating conditions. We also established that the species on the electrode change drastically depending on the oxygen pressures. We used this knowledge to clarify that the favored ORR pathway is dependent on the operating conditions, thus identifying a key parameter to be controlled in high efficiency fuel cells [2].

1. S. Kaya, H. Ogasawara, L.-A. Nasdslund, J.-O. Forsell, H. Sanchez Casalongue, D.J. Miller, A. Nilsson, Ambient-pressure photoelectron spectroscopy for heterogeneous catalysis and electrochemistry, Catalysis Today 205 (2013) 101.

2. H.S. Casalongue, S. Kaya, V. Viswanathan, D. Miller, D. Friebel, J.K. Noskov, A. Nilsson, H. Ogasawara, Direct observation of the oxygenated species during oxygen reduction reaction on a Pt fuel cell cathode, submitted.

9:20am **IS+AS+SS-ThM5 Ambient Pressure Photoelectron and Electron Spectro-Microscopy Using Electron Transparent Membranes**, *A. Yulaev*, Southern Illinois University Carbondale, *M. Amati, L. Gregoratti*, Sincrotrone Trieste, Italy, *S. Guenther*, Technical University Muenchen, Germany, *M. Kiskinova*, Sincrotrone Trieste, Italy, *I. Sgura, B. Bozzini*, University of Salento, Italy, ***A. Kolmakov***, Southern Illinois University Carbondale

Truly *in situ* (photo-) electron spectroscopy and microscopy under ambient pressure conditions in different environments such as electrolytes, water, reactive liquids and gases would provide a nanoscopic access to processes taking place at solid-liquid-gas interfaces. However this exciting line of research still remains a challenging experimental task but is strongly demanded by a variety of active research directions *i.e.* in fuel cells, batteries, catalysis, (bio-) medical, automotive, geological, forensic *etc*. To address these needs a number of designs have been developed since nineties to probe the samples in liquid state or gases at sub-atmospheric pressure. In particular, the elevated pressure XPS at liquid solid and liquid-gas interfaces have been demonstrated via development of advanced differentially pumped lens systems for the electron energy analyzer or via liquid micro jets and droplet “trains” methods.

Novel quasi-2D materials such as graphene and its derivatives currently constitute the active source of innovations in electronics, optics, energy harvesting/storage, catalysis and bio-medical applications. When isolated as ultrathin (~0.3-1 nm) membranes, graphene sheets have thicknesses comparable to the effective attenuation length of 200-1000 eV electrons. In addition, these membranes are chemically stable, gas impermeable and mechanically robust. Based on this unique combination of properties and on recent developments in fabrication and transfer protocols we demonstrate the capability to perform XPS and electron microscopy studies of the processes taking place at liquid-solid interface through graphene-based membranes.

9:40am **IS+AS+SS-ThM6 Surface Chemistry over Inverse Model Catalysts under Near-Ambient Pressure**, ***A. Baber***, *K. Mudiyenselage, S. Senanayake, J. Rodriguez, D. Stacchiola*, Brookhaven National Laboratory

The importance of metal–oxide interfaces has long been recognized, but the molecular determination of their properties and role is only now emerging. Atoms with properties ranging from metallic to ionic are available at the metal–oxide interface and create unique reaction sites. We have shown that the activation of an efficient associative mechanistic pathway for the water–gas shift reaction by an oxide–metal interface leads to an increase in the catalytic activity of ceria nanoparticles deposited on Cu(111) or Au(111) by more than an order of magnitude. *In situ* near ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) experiments demonstrated that a carboxy species formed at the interface is the critical intermediate in the reaction. To obtain a complete picture of the morphological and chemical changes occurring during catalytic processes, we investigated the reduction of Cu_2O/Cu(111) under NAP of CO by a combination of *in situ* scanning tunneling microscopy (STM) and XPS to provide insight into the highly reducing environment of the water gas shift reaction on a model oxide surface. Systematic studies allow us to identify intermediate structures and determine how reaction fronts propagate across a surface with atomic scale resolution. Traditionally, STM is used to monitor surface structures and electronic properties, but here we show the surface oxide species can be identified with atomic-scale detail under near ambient pressures.

10:40am **IS+AS+SS-ThM9 Ambient Pressure Photoelectron Spectroscopy using Tender X-ray**, *S. Axnanda, E.J. Crumlin, R. Chang, B. Mao,* Lawrence Berkeley National Laboratory, *W. Stolte,* Lawrence Berkeley National La **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields.

Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using tender X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this meeting, we will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell.

We believe the successful development of hard X-ray APXPS endstation will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

11:20am **IS+AS+SS-ThM11 Novel Developments in Near Ambient Pressure XPS – The Route Towards Standard Analysis Tools in Laboratory Environments**, *A. Thissen,* ***S. Bahr***, SPECS Surface Nano Analysis GmbH, Germany

Modern devices are often only functional in environments far away from ultrahigh vacuum, still being the standard operation conditions for all Surface Science techniques. In parallel the importance of surfaces for the correct device operation is continuously increasing due to miniaturiziation down to the nanoscale. To contribute to advanced materials analysis in future means using Photoelectron spectroscopy combined with Scanning Probe Microscopies and related techniques in the generic or near generic device environments. This means high, elevated or near ambient pressures of defined working gas mixtures, liquid media, potentials or magnetic fields applied. Also extremely low or high temperatures might be necessary. In past all standard Surface Science Techniques did not work under these extreme environments. As a route to in situ sample analysis Near Ambient Pressure XPS has already been used for a longer time with tremendous success. Nowadays steps are made to utilize this analysis technique not only at synchrotrons and in academic environments, but also as standard analysis tools in user friendly laboratory systems. This work summarizes and presents existing solutions nowadays and future development routes to new instruments and materials analysis methods being functional under these working conditions. Opportunities and limits will be discussed. from the perspective of a supplier of scientific instruments. Finally applications, examples and results from existing In situ methods like high pressure treatments cells, complete High Pressure or Near Ambient Pressure Photoelectron Spectroscopy or Scanning Probe Microscopy Systems (NAP-PES or NAP-SPM), liquid and electrochemical cells, Liquid sample “manipulators“, and concepts and status of equipment working in highest or lowest temperatures, high magnetic fields and static or dynamic potentials will be demonstrated.

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