

# Thursday Morning, October 21, 2010

## Energy Frontiers Topical Conference

Room: Pecos - Session EN+AS-ThM

### Surface and Interface Analysis of Materials for Energy

Moderator: S.M. Han, University of New Mexico

8:00am EN+AS-ThM1 **Functionalization of Carbon Materials for the Controlled Deposition of Pt Electrocatalysts for Fuel Cell Applications.** S. Pylypenko, Colorado School of Mines, National Renewable Energy Lab, A. Dameron, T. Olson, K.C. Neyerlin, J. Bult, C. Engtrakul, National Renewable Energy Lab, A. Queen, Colorado School of Mines, K. O'Neill, T. Gennett, H.N. Dinh, B. Pivovar, National Renewable Energy Lab, R.P. O'Hayre, Colorado School of Mines

Catalyst-support interactions are essential in the design of materials for a variety of applications related to renewable energy technologies. In the fuel cell field, improved understanding of these interactions enables controlled improvement in the catalytic activity and durability of carbon-supported fuel cell electrocatalysts. Carbon surface chemistry and structure can be altered to achieve a desired coverage, morphology and composition of the metal nanoparticle. For example, doping a model HOPG surface with argon or nitrogen results in structural and chemical modification of its surface that leads to improved dispersion, decreased nanoparticle phase and, at certain conditions, enhanced stability. In this work, the role of surface defects, oxygen and nitrogen groups introduced during doping and their effect on electrocatalyst deposition and performance is evaluated through a combination of spectroscopic (XPS, Raman, EELS) and microscopic (SEM, TEM) methods. The same methods are used to evaluate the effect of various surface modifications (via Ar plasma, O<sub>2</sub> plasma and their mixture, HNO<sub>3</sub>, TMA functionalization, etc.) on high surface area carbon materials (CNTs, for instance) and their effect on nucleation and growth of Pt in a controlled nanoparticle or continuous coating phase.

8:20am EN+AS-ThM2 **Structural and Morphological Properties of Carbon Supports studied by XPS and SEM: Effect on Catalyst Degradation.** A. Patel, K. Artyushkova, P. Atanassov, University of New Mexico, A. Young, M. Dutta, Z. Ahmad, V. Colbow, S. Wessel, Ballard Power Systems, Canada

Understanding the chemical structure and morphology of Pt electrocatalysts and their supports, and linking these parameters to electrocatalytic activity, corrosion stability and overall performance of the fuel cell is essential for elucidation of failure mechanisms and optimization of support properties. The strategy presented in this work can be viewed as universal methodology that allows correlation between multiple variables relevant to fuel cell technology.

In this work we have investigated the performance and corrosion stability of Pt electrocatalysts supported on different carbon supports in order to understand the effect of the carbon support on catalyst degradation. Low surface area (LSA), mid-range surface area (MSA), high surface area (HSA) and heat treated (to induce graphitization) high surface area carbons were extensively studied and characterized.

X-ray Photoelectron Spectroscopy (XPS) has been chosen to obtain information on graphiticity and amount of surface oxides on carbon supports. The ability to discriminate between different carbon chemical environments, not just elemental compositions, is one of the primary advantages of XPS in the characterization of carbon corrosion.

Morphological properties such as size of particles, size of particles agglomerates, surface area, roughness and porosity are equally contributive to corrosion process. Digital Image Processing (DIP) can be applied to SEM and TEM images to extract statistical parameters, such as roughness, particle size distributions, shape parameters, texture parameters, which all are related to morphology of carbon blacks.

Performance and durability of Pt electrocatalysts supported on various carbon blacks were evaluated extensively electrochemically to provide activity from rotating disk electrode measurements, capacitance and photon resistance from Electrode Impedance Spectroscopy, voltage degradation rates, effective platinum surface area and kinetic losses.

This multi-analytical approach provides a large set of variables (structural, physical and microscopic properties) which must be related to corrosion and performance behaviour of carbon blacks. Multivariate statistical methods of data analysis (MVA) become, thus, of critical importance in structure-to-property relationship modeling. Principal Component Analysis (PCA) is used as a visualization tool to find samples which are globally correlated or anti-correlated, and to facilitate visualization of the variables responsible for the correlations. Through this methodology, we have determined which set

of structural and morphological parameters are responsible for durable and active electrocatalyst.

8:40am EN+AS-ThM3 **Anchoring of N3, N719 and Z907 Dye Molecules on TiO<sub>2</sub>(110) Surface.** P. Nachimuthu, A. Pandey, Z.Q. Yu, Z.H. Zhu, K.M. Beck, S. Thevuthasan, M.A. Henderson, D.R. Baer, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the alignment of the energy levels for the dye and TiO<sub>2</sub> resulting from the electronic coupling between these states determines the photoinduced electron transfer across the dye-TiO<sub>2</sub> interface. The electronic coupling which in turn is strongly modified by the mode of binding of the dye molecules onto TiO<sub>2</sub> surface, its relative orientations and geometrical structures. In order to understand the mode of binding of the dye molecules on TiO<sub>2</sub>(110) surface, the N3, N719 and Z907 dye molecules in the powder form and adsorbed on TiO<sub>2</sub>(110) surface using 0.25-1.0 mg/ml in ethanol were investigated using high-resolution x-ray photoelectron spectroscopy. The S 2p XPS data from N3 dye molecules adsorbed onto TiO<sub>2</sub> surface show two S components in addition to SO<sub>x</sub>, suggesting that the S atoms in the -NCS functional groups exist in two different chemical environments with a binding energy difference of ~1 eV and the intensity ratio of ~1 indicating that in each intact N3 molecule on TiO<sub>2</sub>, one -NCS group is bound to TiO<sub>2</sub>(110) surface and the other is projected away from TiO<sub>2</sub> surface. The O 1s XPS data show components at 531.2 eV and 533.1 eV which are arising from C=O / COO<sup>-</sup> and C-OH bonds from carboxylic acid groups in N3 molecule, respectively, in addition to a peak at 529.7eV from TiO<sub>2</sub>. The relative intensity ratio of the O 1s XPS components at 533.1 eV to 531.2 eV signifies the presence of protonated carboxylic acid groups in N3 molecule and is found to be 0.388 suggesting that only one carboxylic acid group in each N3 molecule is deprotonated and it is most likely bound to TiO<sub>2</sub> surface. In contrast, both the -NCS groups in the N719 and Z907 dye molecules were projected away from the TiO<sub>2</sub> surface and are not involved in binding with TiO<sub>2</sub> surface. One of the carboxylic acid groups in Z907 is deprotonated and it is most likely bound to TiO<sub>2</sub> surface. Furthermore, with decreasing the dye concentration in ethanol results in a gradual dissociation of -NCS groups from Ru in these dye molecules.

9:00am EN+AS-ThM4 **Characterization of Minority Carrier Lifetime in Ge Films Epitaxially Grown on Si by Nanoscale Interfacial Engineering.** J.J. Sheng, D. Leonhardt, University of New Mexico, J.G. Cederberg, M.S. Carroll, Sandia National Laboratories, M.J. Romero, S. Johnston, National Renewable Energy Laboratory, S.M. Han, University of New Mexico

High-quality Ge-on-Si (GoS) heterostructures are pursued for many applications, including near infrared (NIR) photodetectors and integration with III-V films for multijunction photovoltaics. However, such integration poses many engineering challenges, ranging from lattice mismatch, to thermal expansion coefficient mismatch, to non-planar morphological evolution. We have previously demonstrated a scale-up of growing low-dislocation-density Ge on Si by manipulating the Ge-Si interface at the nanoscale, using a thin chemical SiO<sub>2</sub> layer and a surface reaction involving Ge and SiO<sub>2</sub>. We have also developed a slurry-free, chemical-mechanical polish step to planarize the GoS surface resulting in a Ge surface with a root mean square (RMS) roughness of less than 1 nm. Herein, we focus on the characterization of carrier lifetime in the Ge epilayers grown on Si by the said nanoscale Ge-Si interfacial engineering. Using photoconductivity decay techniques, minority carrier lifetime is measured in the GoS substrates to extract surface recombination velocity as well as carrier lifetime in bulk Ge. The effective surface recombination velocity, representing both Ge-Si interface decorated with chemical SiO<sub>2</sub> and Ge surface, is approximately 1.26x10<sup>4</sup> cm/sec, largely dominated by recombinations at the oxide. We observe that the extracted lifetimes, which vary with the Ge film thickness, correlate well with the dislocation density that varies as a function of distance from the Ge-Si interface. In this presentation, we will further discuss capacitance-voltage characterization of metal-oxide-semiconductor structures fabricated on our GoS substrates.

9:40am EN+AS-ThM6 **A Multi-technique Approach to the Characterization of New Materials for Energy Production.** T. Nunny, R.G. White, N. Bulloss, P. Camus, J. Konopka, ThermoFisher Scientific, UK, H.M. Meyer III, Oak Ridge National Laboratory

In order to meet the challenges of more economical and environmentally benign energy production, a new generation of complex materials and devices is being developed, these include thin film solar cells, fuel cells, and batteries. In all stages of development there is a requirement for materials characterization and analysis; from the initial development stages, through to testing of the finished article. Most materials need to be analyzed for

compositional homogeneity across the sample surface and also for layer chemistry, interface chemistry and thickness through the sample. It is rare that a single technique can achieve all of these testing requirements, and therefore a complementary approach involving several techniques is demanded.

In this presentation we will discuss how a multi-technique approach can address a variety of technical problems, illustrated by examples from real applications case studies. We will mainly concentrate on the information supplied from two techniques, XPS and EDS, but we will also consider the additional data that can be obtained from other sources such as Raman spectroscopy.

X-ray photoelectron spectroscopy (XPS) is ideally suited to the quantitative determination of the surface chemistry and the way in which that chemistry changes in the surface, near-surface and interface region of the materials.

Energy Dispersive Spectroscopy (EDS) collects characteristic X-rays generated by rastering an electron beam over a solid sample to generate a full elemental X-ray spectrum at each pixel of the electron image. The latest generation silicon drift detectors for EDS are capable of collecting and storing hundreds of thousands of X-ray counts per second. This large volume of X-ray data, collected across the sample, allows for rapid identification and characterization of surface defects and lateral compositional variations. Software advances now allow rapid, multivariate statistical analysis processing of very limited amounts of X-ray data to determine not only the elemental distribution across the sample but also the chemical phase distribution.

10:40am **EN+AS-ThM9 Novel Visible-Light Photo-Sensitive Zirconium Oxynitride ( $ZrO_xN_y$ ) Thin Films**, C.V. Ramana, N.E. Esparaza, I. Fernandez, University of Texas at El Paso, A.L. Campbell, Wright Patterson Air Force Base

Zirconium oxide ( $ZrO_2$ ) exhibits excellent optical properties such as high refractive index, large band gap, low optical loss, high transparency in the visible and near-infrared regions, and high dielectric constant. However,  $ZrO_2$  is UV-light sensitive. In addition, interfacial reactions during thin-film growth suppress the effective dielectric constant and degrade the optical performances. The present work was performed on  $ZrO_xN_y$  thin films to effectively alter the electronic structure by the method of nitridation, which well-known to suppress the interfacial reactions.  $ZrO_xN_y$  thin films were produced by magnetron-sputter deposition under the reactive pressure of nitrogen and oxygen. The effect of nitrogen/oxygen flow rate on the structure and optical properties of  $ZrO_xN_y$  thin films was investigated and compared with that of  $ZrO_2$ . The optical measurements of  $ZrO_2$  films show a very high optical transmission with a band gap of 5 eV. The optical absorption measurements on  $ZrO_xN_y$  thin films grown at various reactive nitrogen pressures indicate a progressive shift from insulating to semiconductor behavior. The corresponding changes in the profiles of index of refraction were also remarkably distinct. The results indicate that tailoring the electronic structure and optical constants of  $ZrO_xN_y$  thin films to meet the requirements of visible-light functionality can be achieved by carefully controlling the reactive pressure. The results will be presented and discussed in detail.

11:00am **EN+AS-ThM10 Quantification of Hydrogen and Deuterium in Niobium and Niobium Oxide**, P. Maheshwari, F.A. Stevie, North Carolina State University, G.R. Myneni, G. Ciovati, Jefferson Lab, M. Rigsbee, D.P. Griffis, North Carolina State University

Superconducting Radio Frequency (SRF) cavities provide enhanced efficiency and reduced energy utilization in present day particle accelerators. Niobium (Nb) is the material of choice for these cavities due to its high critical temperature and critical magnetic field. In order to understand why certain treatments, especially a low temperature bake, improve performance, it is important to study Nb surface characteristics and identify elemental contamination that can affect the performance of the cavity. H, C, O, and N are of interest because they are interstitial impurities in Nb. In earlier work,[1] SIMS analysis using a CAMECA IMS-6F with  $Cs^+$  primary beam showed that C and N were probably not significant factors impacting performance and that there was a very high level of H in the Nb. TEM analysis also showed that the surface niobium oxide was a uniform layer with typical thickness about 6nm. Ion implants of C, N, O, and D into Nb provided quantification of C, N, O and indicated that D is very mobile in the Nb.[2]

Analysis of samples before and after heat treatment showed that the H level could be dramatically reduced after certain heat treatments. Removal of the oxide with HF caused the H to return to its former level and the native oxide was again established. SIMS measurement of H in the niobium oxide showed a low H level and, as noted above, the oxide appears to be a very effective H barrier. One possible cause for the removal of H by low temperature heat treatment is the possible formation of openings in the oxide barrier which allows the hydrogen to exit the Nb surface, followed by

the renewal of the oxide after heat treatment which does not allow H to re-enter. Another theory is that the heat treatments drive the H deeply into the Nb.

In order to better understand the role of the niobium oxide, implants have now been made into a specially prepared 120nm thick niobium oxide layer on Nb substrate. H is shown to have an implant shape in the oxide and verify that H is not mobile in the oxide. An implant of D with peak at the oxide/Nb interface showed an implant shape up to the interface and a sharp drop once the Nb was reached. If the H relative sensitivity factor from the oxide is used to quantify the H in a Nb sample without heat treatment, the H concentration is measured as  $2E22atoms/cm^3$ .

[1] A. D. Batchelor, D. N. Leonard, P. E. Russell, F. A. Stevie, D. P. Griffis, G. R. Myneni, Proceedings of Single Crystal Niobium Technology Workshop, Brazil, AIP Conference Proceedings, Melville, NY (2007) 72-83.

[2] P. Maheshwari, H. Tian, C. Reece, G. Myneni, F. Stevie, M. Rigsbee, A. Batchelor, D. Griffis, Surf. Int. Anal. (in press 2010)

11:20am **EN+AS-ThM11 Study of Thin Film Solar Cell Materials using Variable-Wavelength Electric Force Microscopy**, J. Luria, J.J. Choi, T. Hanrath, J.A. Marohn, Cornell University

Organic electronics offer a clear path to large scale, low cost photovoltaics. But efficiency issues such as charge transport, extraction, and device degradation keep these materials from being market-viable. Electric Force Microscopy (EFM) allows us to probe electronic properties of various materials and meso-scale morphologies. By observing the photo-induced response and degradation, we are able to inform synthetic and fabrication processes.

We have developed a general approach to illuminate samples in our custom-built vacuum electric force microscope. We will describe experiments using variable-wavelength light to characterize lead sulfide, PFB/F8BT polymer blend, and other thin film photovoltaic devices.

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