

Tuesday Afternoon, October 19, 2010

In Situ Microscopy and Spectroscopy Topical Conference

Room: Acoma - Session IS+SS-TuA

In Situ Microscopy/Spectroscopy – Interfacial Chemistry/Catalysis

Moderator: S. Kodambaka, University of California Los Angeles

2:00pm **IS+SS-TuA1 In-situ LEEM Study of Ceria Growth on Cu(111)**, J.T. Sadowski, S.D. Senanayake, F. Yang, Y.M. Choi, Brookhaven National Laboratory, J.I. Flege, J. Falta, B. Menkens, University of Bremen, Germany, J.A. Rodriguez, J. Hrbek, Brookhaven National Laboratory

The use of CeO₂-based materials in catalysis has attracted considerable attention in recent years. Ceria has shown great potential as a novel reducible oxide support with unique oxygen storage capacity (OSC) [1]. Ceria can accommodate a large number of oxygen vacancies and the oxidation states of the Ce cation can be switched readily between Ce³⁺ and Ce⁴⁺ depending on the ambient conditions. Hence ceria can actively participate in redox chemical reactions.

The formation of well-ordered, flat CeO₂ films is required in order to minimize substrate effects in surface chemistry of ceria. An earlier successful approach to this problem involved growth of ceria films on Ru(0001) [2]. More recently, CeO₂(111) was grown on a Cu(111) substrate [3]. High activity of ceria-based model catalysts was demonstrated on the inverse catalyst [4, 5] with ceria nanoparticles supported on noble metal substrates. Overall, there is still little known about the mechanism for the growth of ceria film on metal surfaces, its structure and stoichiometry.

In the present work the growth of thin ceria films on Cu(111) has been investigated *in-situ* by means of low-energy electron microscopy (LEEM). Ce was deposited from an e-beam evaporator onto Cu(111) under O₂ atmosphere (5x10⁻⁷ Torr). Real-time observation of the film growth revealed that at relatively high substrate temperature (above 800K) flat, highly crystalline, epitaxial CeO_x(111) film has been formed. In this presentation we will discuss in detail the mechanism of the nucleation and growth, and the atomistic structure of the CeO_x film on Cu(111) under varying growth conditions and Cu(111) oxidation state.

[1] A. Trovarelli, *Catalysis by Ceria and Related Metals*, Imperial College Press, London, 2002.

[2] D. R. Mullins, P. V. Radulovic, S. H. Overbury, *Surf. Sci.* **429**, 186 (1999).

[3] V. Matolin, J. Libra, I. Matolinova, V. Nehasil, L. Sedlacek, F. Sutara, *Appl. Surf. Sci.* **254**, 153 (2007).

[4] J. A. Rodriguez, S. Ma, P. Liu, J. Hrbek, J. Evans, and M. Pérez, *Science*, **318**, 1757 (2007).

[5] J. A. Rodriguez, J. Hrbek, *Surf. Sci.*, **604**, 241 (2010).

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2:20pm **IS+SS-TuA2 Quantitative Speciation of Zn(II) During the Solution Synthesis of ZnO Nanowires Using In-Situ XANES Spectroscopy**, K.M. McPeak, Drexel University, M. Becker, B.A. Bunker, University of Notre Dame, J.B. Baxter, Drexel University

Low temperature, aqueous solution synthesis is widely used to deposit ZnO nanowire arrays for applications such as dye sensitized solar cells. Zinc nitrate and hexamethylenetetramine (HMTA) are the most common precursors for the solution synthesis of ZnO nanowires; but after ten years of using this chemistry, the underlying mechanisms of the reaction remain unclear. We report on the in-situ x-ray absorption spectroscopy of ZnO

nanowire growth from HMTA and zinc nitrate precursors. Time-resolved, in-situ x-ray absorption near-edge structure (XANES) spectra, at the Zn K-edge, give detailed information about the local structure of both Zn(II) in solution and the solid phases formed throughout the reaction. A principal component analysis (PCA) algorithm was employed to determine the number and type of probable species present during the growth of ZnO nanowires under real reaction conditions, with temperatures up to 90 °C and concentrations ranging from 4 – 25 mM. Only two species were present for ZnO nanowire growth at all concentrations and temperatures studied: [Zn(6H₂O)]²⁺ and ZnO_(s). The proportions of these Zn species as a function of reaction time were determined quantitatively by least-squares fitting (LSF) the experimental time-dependent XANES spectra with linear combinations of the principal component spectra. PCA and target testing conclusively refute previous theories that ZnO nanowire growth from HMTA and zinc nitrate precursors occurs due to the thermal decomposition of an intermediate zinc-amine or zinc-HMTA complex. Additionally, XANES analysis shows that no zinc hydroxide intermediates exist above the detection limit of 0.05 mM. Beyond the focused investigation of ZnO, this study also establishes in-situ XANES spectroscopy, in combination with PCA and LSF, as an excellent quantitative tool to understand the solution synthesis of semiconductor nanostructures and thin films.

2:40pm **IS+SS-TuA3 X-ray Spectromicroscopy of Organic and Inorganic Nanostructures**, S.G. Urquhart, University of Saskatchewan, Canada

INVITED

Understanding the composition and structure of complex surfaces is essential for many scientific questions, from understanding processes in surface corrosion to the development of organic electronic devices. X-ray Spectromicroscopy provides surface sensitive chemical speciation with high lateral spatial resolution, by combining the chemical sensitivity of X-ray absorption and photoemission spectroscopy with the high spatial resolution of X-ray microscopy. This presentation will discuss x-ray spectromicroscopy studies to study phase segregation in mixed Langmuir Blodgett thin films as well as efforts to develop a new zone-plate based surface sensitive spectromicroscopy.

1.) We have used surface sensitive X-ray Photoelectron Emission Microscopy (X-PEEM) to study the mechanisms of phase separation and growth in mixed Langmuir Blodgett thin films.[1,2] Here, the chemical sensitivity of x-ray absorption spectroscopy provides spatially resolved composition information to complement the morphology information provided by AFM.

2.) We are developing of a new form of new surface sensitive x-ray microscopy, based on electron-yield detection in a scanning zone plate microscope. Preliminary results from the development of this new method will be presented.

References:

1.) Christensen et al., *J. Electron Spectrosc. and Rel. Phenom.* (2008) **162**, 107-114.

2.) S.E. Qaqish, *Langmuir* (2009) **25**, 7401-7409.

Research supported by NSERC (Canada) and performed at the Canadian Light Source (CLS) and the Advanced Light Source (ALS). The CLS is supported by NSERC, NRC, CIHR, U. Saskatchewan, and the ALS is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

4:00pm **IS+SS-TuA7 The Use of in-situ Spectro-Electrochemical Tools on the Way to R&D of Rechargeable Li and Mg Batteries**, D.A. Aurbach, Bar-Ilan University, Israel

INVITED

The performance of high energy density rechargeable Li and Li ion batteries depends on passivation phenomena. On thermodynamic basis, both the negative electrodes: Li metal or lithiated carbonaceous materials and the positive electrodes: lithiated transition metal oxides are reactive with the electrolyte solutions that are relevant to these systems (polar-aprotic solvents and Li salts).

Thereby, it is highly important to understand the complicated surface chemistry that characterizes all kinds of rechargeable Li batteries. Based on understanding the correlation between surface phenomena, performance and safety features, it is possible to optimize electrolyte solutions in which irreversible phenomena and electrodes capacity fading will be minimized. Consequently, it was highly important to develop specific spectroscopic and microscopic tools that can be used in conjunction with electrochemical techniques and can be specifically suitable for such highly reactive systems. In this talk we demonstrate the development and use of *in-situ* FTIR spectroscopy for mapping the complicated surface reaction of Li metal electrodes in most relevant electrolyte solutions. Especially important was an approach based on internal reflection modes. The use of *in-situ* Raman spectroscopy for understanding lithiation processes of graphite in ionic liquids will be demonstrated. Application of spectroscopy enables to follow detrimental processes such as co-intercalation of the solvents' cations together with Li insertion, what interferes badly with the passivation phenomena, on which the reversibility and stability of Li-graphite anodes depend. The same techniques were applied to non-aqueous electrochemistry of magnesium, in the framework of R&D of rechargeable Mg batteries. The use of EQCM was helpful in characterizing passivation free Mg electrodes, in ethereal solutions with contain magnesium organo-chloro-aluminate complex electrolytes. Highly useful for the study of surface phenomena related to Li batteries were *in-situ* AFM measurements, with which it was possible to follow delicate phenomena related to surface films formation, exfoliation of Li-graphite electrodes and break down and repair of passivation phenomena on both Li metal and Li graphite electrodes. The study of Mg anodes was nicely promoted by the use of *in-situ* STM measurements. This technique was very suitable for characterization of Mg anodes in passivation free electrolyte solutions. New directions for development of *in-situ* techniques suitable for highly reactive electrochemical systems, will be discussed.

4:40pm IS+SS-TuA9 Electrochemistry Platforms for In Situ Transmission Electron Microscopy of Li-ion Batteries. A. Subramanian, J.P. Sullivan, J. Huang, M.J. Shaw, N. Hudak, Sandia National Laboratories, Y. Zhan, J. Lou, Rice University

Nanoscale materials offer a number of potential advantages for Li-ion batteries: examples include low-cost LiFePO₄ nanoparticle cathodes that exhibit good rate performance despite having low electrical conductivity and high-capacity conversion anodes that have high cycle life despite large volume changes per cycle, e.g. Si nanowires. However, one of the challenges with the use of nanoscale materials is their electrochemical characterization, particularly assessing structural changes in nanoscale particles, or reaction product layer interfaces, such as the solid-electrolyte-interphase (SEI). This requires tools with atomic to nanoscale spatial resolution. To meet this need, we have developed a micro-electromechanical systems (MEMS)-based platform for performing electrochemical measurements using volatile electrolytes inside a transmission electron microscope (TEM). This platform uses flip-chip assembly with special alignment features and multiple buried electrode configurations. The nanoscale materials of interest are assembled into the viewing area using dielectrophoresis (DEP). This permits the incorporation of a diverse array of nanoscale particles, including the co-assembly of anode materials in proximity to cathode materials. As an initial realization of the MEMS-based platform, we have developed an unsealed platform that permits *in situ* TEM electrochemistry using ionic liquid electrolytes or *ex situ* electrochemistry and TEM imaging using conventional battery electrolytes. We have demonstrated these approaches using β -MnO₂ nanowire cathodes that were individually assembled using DEP. These wires were lithiated over a range of potentials, in ethylene carbonate-based electrolytes with lithium metal as a counter electrode, in order to produce a range of lithium content. Using TEM and solid-state electrical characterization, we observed that lithiation introduces increasing lattice disorder particularly at the nanowire surfaces; yet, the wires remain β -phase. The electrical measurements revealed a monotonic decrease in electrical conductivity with increasing lithium content, consistent with electronic localization at defects or an increased band gap. From these results, we conclude that *in situ* TEM characterization tools will enable important mechanistic understanding of Li-ion battery materials. This work was supported by LDRD and EFRC projects and was performed, in part, at CINT, a U.S. DOE, Office of Basic Energy Sciences user facility. Sandia is a multiprogram laboratory operated by Sandia Corp., a wholly owned subsidiary of Lockheed Martin Company, for the U.S. DOE's NNSA under contract DE-AC04-94AL85000.

5:00pm IS+SS-TuA10 In-Situ Heating, Imaging, and Analysis of Nanoparticles Using SEM, STEM, and XPS. J.L. Sturgeon, RJ Lee Group, Inc., Z. Liu, University of Pittsburgh, K.L. Bunker, T.L. Lersch, J. Mastovich, B.R. Strohmaier, RJ Lee Group, Inc., J.C. Yang, University of Pittsburgh

Use of an *in-situ*, semiconductor-based heating stage in high-resolution scanning electron microscope (SEM) and scanning transmission electron microscope (STEM) instruments permits rapid, but controlled, temperature changes and the ability to collect images and videos in real time with minimal drift. A Protochips Aduro™ system utilized on a Hitachi S-5500 SEM/STEM allows analysis at elevated temperatures coupled with low voltage SEM/STEM imaging. Catalyst nanoparticles consisting of an iron core surrounded by a carbon shell have been studied using this technology. Elevated temperatures result in a variety of changes to the core-shell structure as well as migration and agglomeration of the iron nanoparticles. X-ray photoelectron spectroscopy (XPS) was also used to study the surface chemistry of these materials before and after heating. These experiments give critical insights into the kinetics of reaction of the iron nanoparticles. Additional analysis at higher accelerating voltages is possible using a dedicated STEM instrument. Other applications using elevated heating of nanoparticles will be discussed.

5:20pm IS+SS-TuA11 Understanding the Role of Fe Catalyst in Carbon Nanotube Growth Using Atomic-Scale (S)TEM. A. Mkhoyan, M.J. Behr, E.S. Aydil, University of Minnesota

The combination of unique mechanical, thermal, optical, and electronic properties of carbon nanotubes (CNTs) make them a desirable material for use in a wide range of applications. Many of these unique properties are highly sensitive to how carbon atoms are arranged within the graphene nanotube wall. Plasma-enhanced chemical vapor deposition (PECVD) from methane-hydrogen gas mixtures using Fe catalytic nanoparticles enables large-scale growth of CNT films, however, much is still unknown about what happens to the catalyst particle during growth and how it dictates the final nanotube structure. To investigate the fundamental processes of CNT growth by PECVD (S)TEM based characterization techniques were used including convergent-beam electron diffraction (CBED), high-resolution (S)TEM imaging, energy dispersive x-ray spectroscopy and electron energy-loss spectroscopy (EELS).

It is found that hydrogen plays a critical role in determining the final CNT structure through controlling catalyst crystal phase and morphology. A variety of tube structures grow, via a base-growth mode, from single crystalline BCC iron and cementite catalyst particles. At low hydrogen concentrations in the plasma, well-graphitized nanotubes grow from elongated Fe₃C crystals, while at high hydrogen concentrations, poorly-graphitized nanofibers grow from BCC iron crystals. Although catalyst particles are single crystals, they exhibit combinations of small-angle rotations, twists, and bends along their axial length between adjacent locations. Distortions are most severe away from the base up into the nanotube where the number of walls is large. This suggests that the stresses generated by the surrounding nanotube distort the catalyst particle during growth. The much larger thermal expansion coefficient of Fe₃C compared to that of the nanotube may also play a role in shaping the crystal into the observed tear-drop morphology. No preferential catalyst orientation relative to the nanotube axis was observed, suggesting that what is required for nanotube growth is not an epitaxial relationship with the catalyst, but rather, only formation of an initial graphitic carbon seed. Z-contrast STEM images combined with atomic-scale EELS measurements also revealed an iron-oxide shell at the very base of each BCC and Fe₃C catalyst crystal.

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