Monday Afternoon, October 29, 2012

Thin Film
Room: 11 - Session TF+EN-MoA

ALD for Energy
Moderator: R.K. Grubbs, Sandia National Laboratories

2:00pm TF+EN-MoA1 Atomic Layer Deposition for the Synthesis of Nanostructured Catalysts, *J.W. Elam*, C. Marshall, Argonne National Lab, *E. Stach, F. Ribeiro,* Purdue Univ., *J. Greeley,* Argonne National Lab, *J. Notestein, K. Poeppelmeier,* Northwestern Univ., *L. Curtiss,* Argonne National Lab, *M. Kung, P.C. Stair,* Northwestern Univ., *L. Winans,* Argonne National Lab, *S. Nguyen*, Northwestern Univ. **INVITED**
The successful transition to an energy economy based on biomass will require radical advances in catalyst science. This challenge demands a new paradigm in catalyst synthesis whereby inorganic components can be assembled at the atomic scale to yield complex, multifunctional catalysts rivaling Nature's enzymes in their specificity. To this end, we have developed a novel approach combining templated synthesis for shape-selectivity with the atomically-precise positioning of discrete functionalities. In this approach we begin with a supporting scaffold for catalyst growth upon which we chemically attach molecular templates. Next, atomic layer deposition is used to build a structure around each template in an atomically precise, layer-by-layer fashion where the thickness and composition can be tuned at each layer. Finally, the template is removed yielding a "nanobowl" defining a structured catalytic environment. The molecular template can be synthesized to contain bulky organic ligands surrounding a catalytic atom or cluster which remains anchored to the bottom of the bowl after ligand removal. Furthermore, one or more layers in the bowl wall can be selected to serve as a co-catalyst (e.g. Lewis acid group) positioned at a well-defined distance from the catalyst at the bottom of the bowl. This presentation will review our recent progress synthesizing, characterizing, modeling, and testing these unique catalytic materials.

2:40pm TF+EN-MoA3 Using Metalcone Films Grown by Molecular Layer Deposition to Form Conducting Metal Oxide-Carbon Composite Films, *A. Abdulagatov, K. Terauds, J. Travis, A. Cavanagh, R. Raj,* CU Boulder, *S.M. George*, University of Colorado, Boulder
Metalcone films grown using molecular layer deposition (MLD) techniques with metal and organic precursors are metal alkoxide polymers. These hybrid organic-inorganic films can serve as precursors to conducting metal oxide-carbon composite films. In this study, titanicone MLD films were deposited by sequential, self-limiting exposures of $TiCl_4$ and glycerol at 150°C. These films were then annealed in argon at temperatures ranging from 500 to 1200 °C. Under argon, the hydrogen is removed from the hybrid organic-inorganic titanicone films and the carbon remains. Raman spectroscopy measurements showed the progressive growth and sharpening of the D and G signature peaks for graphitic carbon after annealing from 600 to 900 °C. The sheet resistance of the annealed films was also found to progressively decrease with increasing annealing temperature. X-ray photoelectron spectroscopy depth profiling confirmed the presence of carbon throughout the annealed film. X-ray diffraction measurements also observed the formation of rutile TiO_2 diffraction peaks. The annealing of metalcone MLD films in argon is a general method to deposit metal oxide-carbon composite films. Conducting metal oxide-carbon composite films are desirable because many electrochemically important metal oxides have low electrical conductivities. The metal oxide-carbon composite films with graphitic carbon have much higher electrical conductivities that will enable their electrochemical application for Li ion batteries and pseudocapacitance supercapacitors.

3:00pm TF+EN-MoA4 *In Situ* Growth Study and Material Characterization of Plasma-Assisted Atomic Layer Deposition of Palladium, *M.J. Weber*, A.J.M. Mackus, M.A. Verheijen, N. Leick-Marius, A. Bol, W.M.M. Kessels, Eindhoven University of Technology, Netherlands
Palladium thin films are object of great interest in catalysis, as well as in hydrogen sensing, storage and generation. Noble metals such as Palladium are the most effective if deposited as ultrathin films on a large surface area. Atomic layer deposition (ALD) is considered to be the method of choice to grow ultrathin films on various substrates with demanding surface topologies. This contribution will present *in situ* and *ex situ* studies of Palladium films grown by plasma-assisted ALD. The Pd films were deposited on alumina at 100ºC using Pd(hfac)2 (hfac= hexafluoroacetylacetonate) as the precursor, and H2 gas and H2 plasma as reducing agents. *In situ* spectroscopic ellipsometry (SE) has been used to monitor the film growth and obtain detailed information about the optical properties of Palladium. The nucleation and subsequent island growth have been characterized by Transmission Electron Microscopy (TEM). X-Ray diffraction, X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry have been carried out in order to characterize the grown films. The thermal ALD process only allowed for growth of Pd on a Pd or Pt seed layer, while the plasma-assisted ALD process also led to growth on an alumina surface. In both cases the steady-state growth rate was ~ 0.17 Å/cycle as determined by *in situ* SE. The observed selective growth on catalytic Pd or Pt seed layer of the thermal process holds promises for nanopatterning applications, whereas the plasma-assisted process can be used to deposit Pd nanoparticles and films at low-temperature on oxide substrates, which has considerable potential for catalysis and hydrogen sensor applications.

3:40pm TF+EN-MoA6 ALD-enabled Nanostructures for High Rate Li-ion Storage, *X. Chen*, H. Zhu, L. Hu, G.W. Rubloff, University of Maryland
A major challenge for Li-ion batteries is to achieve high rates (power) by overcoming the long charge/discharge time caused by low Li diffusivity in active storage materials. Nanostructured electrodes provide a potential solution by reducing the thickness of active storage layers, since the diffusion time is proportional to the square of diffusion length. Our strategy to improve the rate performance of Li-ion battery is to use atomic layer deposition (ALD) to grow thin active battery materials on highly conductive current collecting scaffolds with high surface area. The unprecedented conformality of ALD allows maximum utilization of high surface area, while the highly conductive scaffold facilitates easy electron transport and Li^+ migration in electrolyte as also needed for high power. We report two embodiments of this heterogeneous nanostructure configuration, both with ALD V_2O_5 storage layers.

First, we used highly porous multiwall carbon nanotube (MWCNT) sponge as the scaffold. The V_2O_5-MWCNTcoaxial sponge achieves a stable high areal capacity as 816 µAh/cm^2 over voltage range 4.0-2.1 V at current density of 1.1 mA/cm^2 (i.e., 1C rate). This capacity is 450X that of a corresponding planar V_2O_5 thin film cathode. For the same voltage range but 50X higher current, the areal capacity of the V_2O_5-MWCNT sponge is 155 µAh/cm^2, giving a high power density of 21.7 mW/cm^2. The areal capacity increases further to 1284 µAh/cm2, when cycled over a larger voltage window (4.0-1.5 V), but this incurs deteriorated cycling performance as expected from the intrinsic properties of V_2O_5.

Second, we employed well-ordered anodic aluminum oxide (AAO) templates to with ALD current collecting layers as a scaffold for the storage material. ALD TiN was first deposited into the AAO nanopores to form current collecting nanostructures, after which ALD V_2O_5 was deposited on TiN as the active Li storage medium, with both layer thicknesses precisely controlled and highly conformal. The resulting structures, with electrolyte filling the remaining pore volume, provide test structures to understand regimes where either Li+ transport or electron transport can be rate-limiting.

4:00pm TF+EN-MoA7 Enhancement of the Heat Recovery Mechanism in Infrared Photovoltaic Devices Promoted by Thin Planar ALD Oxide Films, *A.J. Vincent-Johnson, H.S. Mann, Y. Schwab,* James Madison University, *A.E. Masters,* Custom Thermoelectrics Inc., *X. Hu, G. Scarel*, James Madison University
Infrared photovoltaic devices absorb infrared radiation and transform it into electricity through the heat recovery mechanism [1,2]. In thin planar oxide films, the mechanism is mediated by the excitation of radiative polaritons, as shown by investigations carried out immediately after beginning the exposition to infrared radiation [1,2]. Here we present the results of our investigation on the evolution of the heat recovery mechanism; and the electricity production over time through illumination by infrared radiation. We compare the results on systems including atomic layer deposited (ALD) Al_2O_3, Al foil, and the bare thermoelectric power generator used for the detection of the heat recovery mechanism. We show that ALD oxide films promote the largest amount of electricity production under long term exposition to both polarized and non-polarized infrared radiation.

[1] A.J. Vincent-Johnson, K.A. Vasquez, J.E. Bridstrup, A.E. Masters, X. Hu, and G. Scarel, Appl. Phys. Lett. **99**, 131901 (2011).

[2] A.J. Vincent-Johnson, A.E. Masters, X. Hu, and G. Scarel. Submitted.

4:20pm TF+EN-MoA8 Ultra-thin TiO_2 Blocking Layer by Atomic Layer Deposition for Dye-Sensitized Solar Cells, *D.H. Kim*, M. Woodroof, K.M. Lee, B. Kalanyan, G.N. Parsons, North Carolina State University
In dye-sensitized solar cells (DSSCs), one of major recombination routes occurs at the interface of fluorine-doped tin oxide (FTO) glass and

electrolyte solution. Typically, a thin and compact blocking layer (B/L) on the FTO-glass has been introduced to reduce electron loss before mesoporous TiO_2 layer integration. A variety of deposition methods have been tried and studied to make efficient B/L on the FTO-glass. Optimal thickness that suppresses the recombination on the interface of FTO glass and electrolyte, is typically 25 to 450 nm, depending on deposition methods and conditions. Compared to other methods, atomic layer deposition (ALD) with TiO_2 is not well established and investigated for blocking layers even though it is a valuable process in making pin-hole, crack-free, and dense TiO_2 films.

In this study, ALD TiO_2 was performed on FTO-glass with titanium isopropoxide and H_2O as precursors, producing B/L thickness from 5 to 100 nm. Cells without mesoporous titania but with ALD TiO_2 B/L were also made. We find the optimal thickness of the ALD TiO_2 blocking layer is 10 nm. This blocking layer thickness significantly reduces recombination, resulting in an average overall efficiency of 8.5%, compared to 7.1% for similar cells without the blocking layer present. We also find that a blocking layer of 4.3 nm effectively prevents electrons of FTO surface from recombining with I_3^- in the electrolyte. On the other hand, a thick ALD TiO_2 blocking layer in excess of 10 nm tended to reduce the overall efficiency because the thick ALD TiO_2 film increases the charge transfer resistance and hinders the electron transport to FTO-glass. This work contributes to understand effective blocking layer from TiO_2 ALD process for DSSCs and other high-performance electrical devices

Authors Index
Bold page numbers indicate the presenter