

Monday Morning, October 28, 2013

Thin Film

Room: 104 A - Session TF+EN-MoM

ALD for Energy

Moderator: W.M.M. Kessels, Eindhoven University of Technology, Netherlands

8:20am **TF+EN-MoM1 Thin Film Electrolyte via Atomic Layer Deposition for Low Temperature Solid Oxide Fuel Cells**, *G. Cho, S. Cha, J. Paek, J. Park, I. Change*, Seoul National University, Republic of Korea **INVITED**

Solid Oxide Fuel Cells (SOFCs) were considered most promising solutions for the next generation power generator. SOFCs usually operate at high temperature due to poor ionic conductivity of their oxide electrolyte. This high operation temperature caused many drawbacks like requirement of high cost thermal-resistive materials, thermal degradation and long start-up time.

There were many investigations to lower the operation temperature of SOFCs to solve aforementioned drawbacks. Among many researches to lower operation temperature, thin film SOFCs showed most impressive outcomes. The thickness reduction of oxide electrolyte by thin film technique led to the ohmic resistance reduction and low operation temperature of SOFCs. Due to thin electrolyte, thin film SOFCs showed high performance at low temperature. Thin film SOFCs were fabricated by thin film technique, i.e. sputter, pulsed laser deposition (PLD), chemical vapor deposition (CVD), atomic layer deposition (ALD) and etc.

The ALD was an advanced thin film technique for various applications. The unique characteristic of ALD, self-limiting growth, led to many advantages, i.e. precise thickness control, excellent step coverage, film uniformity and large area capability. In thin film SOFCs, very uniform and conformal thin film electrolyte was prepared by ALD to remove pin-holes and defects in electrolyte. Most well known materials of electrolyte for SOFCs, Ytria-Stabilized Zirconia (YSZ) was successfully fabricated by combination of deposition processes for Y_2O_3 and ZrO_2 of ALD.

In this research, we prepared thin film YSZ electrolyte for LT-SOFCs via ALD and applied to LT-SOFCs. First, chemical and physical characteristics of thin film YSZ related with different deposition conditions were investigated to confirm the most appropriate YSZ electrolyte for LT-SOFCs. After investigations of thin film YSZ electrolyte, LT-SOFCs with ALD-fabricated YSZ electrolyte were prepared. Nano-porous Anodizing Alumina Oxide (AAO) template was used as the supported structure. Platinum was used for both anode and cathode catalyst to suppress activation loss and current collection resistance. Then, effects of different ALD-fabricated thin film YSZ electrolyte to LT-SOFCs, i.e. open circuit voltage, power density, and electrochemical impedance spectroscopy were investigated.

9:00am **TF+EN-MoM3 Coaxial ALD Nanotube Structures for Functional Nanopore Battery**, *C. Liu, X. Chen, M. Schroeder, K. Gregorczyk*, University of Maryland, College Park, *S.B. Lee*, University of Maryland, College Park and Korea Advanced Institute of Science and Technology, *G.W. Rubloff*, University of Maryland, College Park

Nanowire arrays improve ion access and transport to utilize electrode materials, but the potential power-energy advantage of nanostructuring also requires fast electron transport to the ion storage material throughout high-aspect ratio nanowire geometries. To realize this for high performance nanostructured energy storage, we fabricated uniformly aligned arrays of core-shell nanotube devices (half-cells) by atomic laser deposition (ALD) into anodic aluminum oxide (AAO) templates, using ruthenium (Ru) metal as current collecting layer and then crystalline V_2O_5 as active battery material to form composite nanoelectrodes penetrating part way into the AAO nanopores. The extraordinary conformality of ALD enables controlled formation of the coaxial electrode, with highly conductive Ru metal providing fast electron transport to overlying V_2O_5 storage material.

The 3-D V_2O_5 -Ru coaxial nanocathode array was configured as a half-cell, with $LiPF_6$ based organic electrolyte in the nanopores and a separator and Li anode incorporated into a coin cell. A high specific capacity of 172 mAh/g was measured at 1C rate over the voltage range 4.0-2.6 V corresponding to 1 Li per V_2O_5 . The areal capacity of 59 uAh/cm² was 46X that of a planar V_2O_5 thin film cathode. Excellent cycling performance was demonstrated by capacity retention of 79% after 1000 cycles. Energy density was maintained well at high power – 129mAh/g at 50C rate and 82mAh/g at 200C rate, corresponding to 21 and 52 kW/kg power respectively. Cyclic voltammetry indicates that the capacity at high rate is dominated by double-

layer capacitance rather than intercalation processes. The crucial role of electron transport was illustrated by the 4X reduction in capacity - even at 1C rate - when the 15um deep Ru current collector was replaced by a 0.6um TiN. Part of this difference may be the absence of the TiN current collector adjacent to most of the V_2O_5 storage layer.

9:20am **TF+EN-MoM4 Engineering Lithium-Containing Ionic Conductive Thin Films by Atomic Layer Deposition for Lithium-ion Battery Applications**, *J. Cho, Y. Perng, D. Membreno, N. Cirigliano, B. Dunn, J.P. Chang*, UCLA

Lithium (Li)-ion batteries have drawn much attention for their outstanding performance in portable electronic applications with the potentials to function as a power source for further miniaturized devices including micro-systems through the utilization of 3-dimensional electrodes based on high aspect ratio pillars. To fully utilize such potential, however, an ultra-thin and highly conformal electrolyte layer is required to coat the 3D electrode array. The solid oxide Li-ion conductors lithium aluminosilicate (LASO) synthesized by atomic layer deposition (ALD) are promising electrolyte materials for 3D battery applications not only due to their adequate ionic conductivities for electrolyte applications in Li-ion microbatteries and improve the cell cycling stability upon coating these ultra-thin metal-oxide films synthesized via ALD directly on electrodes.

The self-limiting characteristic of ALD allows for precise control of thickness and composition of complex oxides and results in a highly conformal and pinhole-free coating suitable in 3D micro-battery applications or electrolyte surface coatings. The metal precursors used in this work are tetraethyl orthosilicate (TEOS), trimethylaluminum (TMA) and lithium t-butoxide (LTB). These precursors, along with water vapor as the oxidant, were used to deposit Li_2O , Al_2O_3 , and SiO_2 with the deposition rates in the range of 0.8~2Å/cycles. The deposition rate of stoichiometric $LiAlSiO_4$ was ~20Å/cycle at a temperature of 290°C. The concentration of each metal element in $Li_xAl_ySi_zO$ (LASO) was found to correlate closely to ALD cycles of the constituent oxides. Based on this class of material and the change in the Li to Al(Si), thin films of LAO, LSO and LASO are synthesized to assess the effect of materials' composition and structure. The as-deposited materials were amorphous and the crystallinity of the LASO/LAO/LSO films after post-deposition rapid thermal annealing (RTA) was found to be a function of cation atomic percentage. Li-ionic conductivities and the activation energy of as-deposited LASO/LAO/LSO films with respect to lithium contents and the film thickness were studied.

The detection and characterization of pinholes on the deposited LASO/LAO/LSO films were investigated by cyclic voltammetry. Lithiation cycling tests of thin LASO/LAO/LSO films were found to be both functions of composition and thickness. The reversibility and kinetics of insertion as well as cycling stability enhancement effects from the direct deposition of LASO/LAO/LSO on 2D and 3D electrode materials such as carbon and porous silicon anodes were investigated as a half-cell.

9:40am **TF+EN-MoM5 Manganese Oxide Pseudocapacitive Supercapacitors from Electrochemical Oxidation of MnO ALD Films**, *M.J. Young, C.B. Musgrave, S.M. George*, University of Colorado, Boulder

Pseudocapacitive supercapacitors are a class of electrochemical storage device based on Faradaic charge transfer at the electrode/electrolyte interface. These supercapacitors exhibit higher energy density than electric double-layer capacitors and higher power density than Li ion batteries. Manganese oxide is a well-known pseudocapacitance material. In this work, MnO atomic layer deposition (ALD) was used to study manganese oxide as a pseudocapacitive supercapacitor. MnO ALD films were grown using sequential exposures of $Mn(EtCp)_2$ and H_2O on conducting stainless steel substrates. The MnO ALD films were then oxidized electrochemically to produce oxidized MnO_{1+x} films. The electrochemical capacities of these films were measured using cyclic voltammetry. Capacities were found to increase from capacities of ~80 F/g for the as-deposited MnO ALD films to capacities of ~200 F/g after oxidation. These capacities after oxidation are comparable with the reported capacities of 150-250 F/g for α - MnO_2 which is the crystalline phase of manganese oxide with the highest reported pseudocapacitance. The electrochemical capacity of manganese oxide is not purely a surface effect in contradiction with previous reports in the literature. The results suggest an optimal manganese oxide thickness for the highest specific capacity.

10:00am **TF+EN-MoM6 Low Temperature Atomic Layer Deposition Processes for Flexible Dye-Sensitized Solar Cells**, *M. Creatore, D. Garcia-Alonso, A.J.M. Mackus*, Eindhoven University of Technology, Netherlands, *V. Zardetto, T.M. Brown*, University of Rome "Tor Vergata", Italy, *W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Atomic Layer Deposition (ALD) has been applied to different photovoltaic technologies, including Dye-Sensitized Solar Cells (DSCs), due to its exceptional control of film thickness and composition, high conformality on high aspect ratio structures and uniformity. Thermal ALD for DSCs has been employed to deposit metal oxides for passivation layers on mesoporous TiO₂ photoelectrodes and recombination blocking layers (TiO₂ and HfO₂) on TCOs. In this work, we investigate other potential benefits of ALD not yet applied to DSCs. Low temperature processing by plasma-assisted ALD (PA-ALD) has been successfully applied in flexible DSCs to deliver the synthesis of nano-particles (NPs) for the Pt counter-electrode, and the deposition of compact layers. We demonstrate the potential of low temperature PA-ALD processes to deposit metallic Pt NPs on PEN/ITO substrates with the control in particle size. The counter-electrode (CE) layer (for back-side illumination) requires high transparency and small, evenly distributed particles to enhance its catalytic activity. Two newly developed PA-ALD processes were applied for the deposition of Pt CE layers at 150 °C. The Pt CE electrocatalytic activity towards the iodine-based electrolyte was analysed by electrochemical impedance spectroscopy (EIS). Pt CE layers deposited by both processes exhibit similar transmittance for less than 100 ALD cycles while the charge transfer resistance (R_{CT}) values show a significant difference for a number of ALD cycles lower than 50. Pt layers deposited using between 50 and 150 cycles yielded the best compromise between R_{CT} and transparency, and fulfil the requirements for back-side illuminated DSCs, allowing for an efficiency of 3.5%. When compared to sputtered or electro-deposited Pt layers, the PA-ALD Pt NPs lead to higher solar cell efficiency due to the enhancement in J_{SC} and V_{OC} because of the increased number of photons reaching the active material due to the higher Pt ALD layer transmittance. We also used PA-ALD to successfully deposit TiO₂ compact layers and ultra-thin dielectric Al₂O₃. The aim of these layers is to decrease the recombination processes at the interface between the PEN/ITO substrate and the mediator (liquid electrolyte or organic material), especially at low light intensity, and thus to increase the performance of flexible DSCs for indoor applications. Both compact layers reduce the recombination path at the TCO/electrolyte interface without any effect on the electron collection (EIS analysis). The compact layers improve the generated power as compared to a compact layer-free DSC (Al₂O₃: +26% and TiO₂: +40 %) under low level illumination (300 lux, CFL lamp).

11:00am **TF+EN-MoM9 Performance of ALD Oxide Films in Polarized Infrared Power Generation**, *G.S. Scarel, Y. Schwab, H.S. Mann, B.N. Lang*, James Madison University, *J.L. Lancaster*, University of North Carolina at Greensboro, *R.J. Parise*, Parise Research Technologies

Currently there is a large demand for alternative sources of clean, inexpensive, renewable energy. Solar radiation is very promising in this context. While the visible and near infrared (NIR) portions of the solar radiation spectrum are receiving much attention, thus far little work has been devoted to harvesting and transforming the middle and far (MIR and FIR) regions of the infrared (IR) portion of the spectrum. Here we describe the principle of IR power generation, which transforms IR radiation into electricity using a power generator (PG). While the physical mechanism of IR power generation is not yet fully understood, there is a clear indication that the termination of the external surface of the hot junction of the PG can be used to tune the electricity that is produced. The hot junction of the PG is usually made of a thin copper substrate with about a 1 mm thick alumina ceramic material on the external surface exposed to the IR radiation which absorbs on average about 60 % of the incident IR energy [1]. By terminating the hot junction with a spectrally black surface (emissivity approaching 1.0), this percentage can be greatly enhanced. Also, radiative polaritons [2] in thin alumina films on metallic, semiconducting, and insulating coatings further contribute to absorbing the IR radiation [1]. Thus, a 250 nm thick Al₂O₃ film deposited using atomic layer deposition (ALD) on Al foil placed on the hot junction of the PG can tune the response of IR power generation [3]. The behavior of voltage difference as a function of time measured with non-polarized IR radiation at variable incidence angle q_0 to the normal of the hot junction of the PG was recently published [3]. The presentation here will summarize the first results of the polarized IR power generation obtained from the 250 nm thick ALD Al₂O₃ films on Al foil. Finally, the future technological and scientific challenges for IR power generation using PGs, such as the development of Nighttime Solar Cells® [4] and the discovery of the physical mechanism, will be briefly summarized.

[1] A.J. Vincent-Johnson, K.A. Vasquez, G. Scarel, J.S. Hammonds, and M. Francoeur, *Appl. Spectrosc.* **66**, 188-197 (2012).

[2] A.J. Vincent-Johnson, Y. Schwab, H.S. Mann, M. Francoeur, J.S. Hammonds, and G. Scarel, *J. Phys.: Condens. Matter* **25**, 035901 (2013).

[3] A.J. Vincent-Johnson, K.A. Vasquez, J.E. Bridstrup, A.E. Masters, X. Hu, and G. Scarel, *Appl. Phys. Lett.* **99**, 131901 1-3 (2011).

[4] R. J. Parise and G. F. Jones, Collection of Technical papers – 2nd International Energy Conversion Engineering Conference, 1172–1181 (2004).

11:20am **TF+EN-MoM10 Synthesis of Pd and Pt Nanoparticles by Atomic Layer Deposition for Catalysis Applications**, *M. Weber, M.A. Verheijen, A.A. Bol, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Noble metal nanoparticles (NPs) are known to be very efficient catalysts and are of crucial importance to pharmaceutical, (petro)chemical and environmental industries. Although ALD was primarily developed to deposit conformal thin films, metals have the tendency to form nanoclusters on the substrate during the initial cycles of the process. Using this Volmer-Weber growth mode, Pd and Pt NPs supported on Al₂O₃ were synthesized with the aim to design efficient model catalysts systems. The Pd process was based on Pd(hfac)₂ (hfac= hexafluoroacetylacetonate) as the precursor, and H₂ plasma as co-reactant, whereas the Pt process was carried out with the use of MeCpPtMe₃ and O₂ plasma. The deposition temperature was 100°C. The Pd and Pt NPs resulting from the ALD nucleation stage have been characterized by High Angle Annular Dark Field Transmission Electron Microscopy (HAADF-TEM). High density values of ~10¹² NPs/cm² and narrow size distribution (in particular for Pd) of 2-3 nm NPs have been obtained on alumina substrates, and depositions carried out with one year time interval have shown excellent reproducibility. The tailoring of such NPs by changing the ALD process parameters in order to obtain different particle sizes and composition is also demonstrated. Furthermore, preliminary experiments have shown that these noble metal NPs are efficient as photocatalysts and towards the CO-oxidation. These results open up prospects in the engineering of metallic nanoparticles for fuel cells and micro-reactors applications, for which ALD can be feasible.

11:40am **TF+EN-MoM11 In Situ Characterization of Plasma-Assisted Pt ALD on W ALD Adhesion Layers with Spectroscopic Ellipsometry**, *A.S. Cavanagh, L. Baker, J. Clancey, J. Yin*, University of Colorado at Boulder, *A. Kongkanand, F.T. Wagner*, General Motors Research and Development, *S.M. George*, University of Colorado at Boulder

Platinum is an excellent catalyst for many applications. The high cost of Pt requires that Pt be used as efficiently as possible. For the oxygen reduction reaction in H₂ fuel cells, experiments show that a continuous Pt film is 5-10 times more active per Pt surface atom than a 3 nm Pt nanoparticle. Consequently, understanding the process conditions under which thin continuous films of Pt can be deposited is critical.

Pt has a high surface energy of ~2.5 J/m and does not readily wet most substrates which typically have much lower surface energies. Pt nanoparticles are generally formed during Pt atomic layer deposition (ALD) on oxide substrates. A continuous Pt film is possible only after the coalescence of the Pt nanoparticles. The result is a thick Pt film and the inefficient use of Pt resulting from the thickness.

One possible route to obtain a continuous and ultrathin Pt film is to deposit on an adhesion layer that has a higher surface energy than Pt. In this case, the Pt should wet the adhesion layer because the deposited Pt film will lower the surface energy. One material that has a higher surface energy than nearly all other metals, including Pt, is W. The surface energy of W is ~3.5 J/m.

In situ spectroscopic ellipsometry (SE) allowed for the characterization of Pt ALD nucleation on W ALD adhesion layers. *In situ* measurements of nucleation during plasma-assisted ALD provided rapid feedback on the process variables including plasma power, plasma exposure time and the process gas mixture. *Ex situ* characterization with X-ray photoelectron spectroscopy and X-ray reflectivity was used to verify the SE models employed during *in situ* monitoring of the nucleation of plasma-assisted Pt ALD.

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