Monday Morning, October 30, 2017

Thin Films Division
Room: 20 - Session TF+EM-MoM

ALD for Energy Conversion, Storage, and Electrochemical Processes
Moderator: Mark Losego, Georgia Institute of Technology

8:20am **TF+EM-MoM1 Synthesis and Characterization of All Solid-State SnO$_x$N$_y$/LiPON/Li Batteries**, *David Stewart, A.J. Pearse, K. Gregorczyk, G. Rubloff*, University of Maryland, College Park
Atomic layer deposition (ALD) is excellent for depositing conformal thin films on high aspect ratio substrates, and due to the good thickness control and uniformity, ALD allows us to push the limits of thin film batteries. To produce solid-state lithium ion batteries on such substrates new processes for anodes, high-capacity cathodes, and solid-electrolytes must continue to be developed and characterized. Sn and SnO$_2$ have been well studied as alloy/conversion electrodes in the literature, while the properties of Sn$_3$N$_4$ and SnO$_x$N$_y$ have yet to be explored in any detail. To study the differences in the electrochemical performance of SnO$_2$, Sn$_3$N$_4$, and SnO$_x$N$_y$, an ALD process was developed that allows for highly tunable N/O ratios. In this study tetrakis(dimethylamido)tin (TDMA(Sn)) was used as the metal-organic precursor in combination with remote nitrogen plasma (^{p}N) and H$_2$O was used to introduce oxygen content. For the pure nitride phase, a broad temperature window was found between 150-250 °C, over which the growth rate per cycle (GPC) was ~ 0.55 Å. While only very short pulse times (< 1 s) were required for saturation of the TDMA(Sn), relatively long ^{p}N exposures (> 20 s) were required for GPC saturation. We then showed that by varying H$_2$O super cycles the relative concentration of O and N in the film can be controlled between 0% N and 95% N.

To study the electrochemical performance of these materials solid-state half-cells were constructed using SnO$_2$, Sn$_3$N$_4$, and SnO$_x$N$_y$ thin films versus thermally evaporated Li. A 100 nm thin film of LiPON was deposited as the solid electrolyte by thermal ALD [1]. This electrolyte layer is thick enough to provide good electrical insulation and thin enough to allow fast ionic diffusion, however when cycled to voltages below 0.4 V vs Li/Li$^+$ the half-cells shorted, possibly due to mechanical breakdown of the LiPON layer from significant volume expansion of the anodes during the alloying reaction with Li. The Li$_2$O matrix formed from SnO$_2$ is expected to be more stable, but with lower ionic conductivity than the Li$_3$N matrix formed from Sn$_3$N$_4$. Galvanostatic intermittent titration and electrochemical impedance spectroscopy were used to analyze the ionic conductivity of the anodes before and after the initial conversion reaction and as a function of N/O ratio. The high capacity of the SnO$_x$N$_y$ electrodes in combination with the excellent ionic conductivity and mechanical properties of the ALD LiPON makes these films attractive for applications in 3D Li-ion batteries.

[1] A. J. Pearse, T. E. Schmitt, E. J. Fuller, *et. al.* Chemistry of Materials **2017** *29* (8), 3740-3753 DOI: 10.1021/acs.chemmater.7b00805

8:40am **TF+EM-MoM2 Molecular Layer Deposition for Applications in Lithium-Ion Batteries**, *K. Van de Kerckhove, F. Mattelaer, J. Dendooven, Christophe Detavernier*, Ghent University, Belgium
Molecular layer deposition (MLD) of hybrid organic-inorganic thin films called *titanicones*, *vanadicones*, *tincones*, and *alucones* was investigated for electrode and solid electrolyte applications in lithium-ion batteries.

The titanicone, vanadicone and tincone films were studied as electrode materials, both as anodes and cathodes. Novel MLD processes were developed for these materials and were based on an alkylamine metal precursor (TDMAT, TEMAV, TDMASn) and glycerol (GL) as the organic reactant [1,2]. Linear and self-limited growth could be achieved for these metalcones in a broad temperature range with temperature-dependant growth rates ranging from 0.2 to 1.3 Å/cycle. Film growth was studied in situ with spectroscopic ellipsometry (SE) and infrared spectroscopy (FTIR). The as-deposited films appeared to be electrochemically inactive in all cases. A post-deposition heat treatment up to 500°C in either inert (helium) or oxidizing (air) atmosphere was able to electrochemically activate the films. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements showed that all carbon was removed during calcination in air and that the films crystallized. However, annealing in inert atmosphere conserved the carbon content of the film and thus the films remained amorphous. The performance with increasing charging and discharging rate, and cyclability of the heat-treated MLD electrodes was tested against their respective metal oxide references. The He-annealed metalcones emerged from these tests as the best performing electrodes at higher rates and with improved capacity retention and stability during repeated charging and discharging.

The transformation of alucone films, deposited with the TMA and ethylene glycol (EG) or GL process, into porous aluminium oxide was examined. Porous, non-conducting materials are interesting for lithium-ion battery research since they may serve as the matrix template for solid composite electrolytes. Calcination in air and water etching proved to be the most successful methods. For the calcination treatment, a clear relation was found between the ramp rate during both heating and cooling and the resulting porosity of the film. The aging behaviour of the films in ambient atmosphere was also investigated with FTIR and showed that the films deposited with EG decompose in a matter of only a few hours, as opposed to those deposited with GL.

[1] Van de Kerckhove et al., *Dalton Trans.*, 2016,**45**, 1176-1184.

[2] Van de Kerckhove et al., *Dalton Trans.*, 2017,**46**, 4542-4553.

9:00am **TF+EM-MoM3 Engineering Hybrid Thin Film Electrolytes for 3D Lithium-ion Battery Applications**, *Ryan Sheil, J. Lau,* University of California at Los Angeles, *P. Moni,* MIT, *C. Choi,* University of California at Los Angeles, *K. Jungjohann,* Sandia National Laboratories, *J. Yoo,* Los Alamos National Laboratory, *K. Gleason,* MIT, *B. Dunn, J.P. Chang*, University of California at Los Angeles
3D battery architectures have the potential to meet the power and energy density demands of next generation microelectronic devices. One requirement in the utilization of 3D based electrodes is the incorporation of a solid electrolyte that can be coated pinhole free and conformally on high aspect ratio structures. Lithium aluminosilicate (Li$_x$Al$_y$Si$_z$O, LASO), a solid oxide Li-ion conductor, synthesized by atomic layer deposition (ALD) is a promising electrolyte material for 3D battery applications due to its adequate ionic conductivity (8.2×10^{-8} S/cm) in thin film applications as well as its ability to improve electrode stability. The self-limiting nature of ALD allows precise thickness and composition control when applied to complex metal oxides. Lithium tert-butoxide (LTB), trimethylaluminum (TMA), and tris(tert-butoxy)silanol (TTBS), were precursors used to synthesize LASO by ALD.

In order to further explore potential material properties, ALD deposited LASO was combined with a polymer electrolyte, poly-(tetravinyltetramethylcyclotetrasiloxane) (PV4D4) deposited via initiated chemical vapor deposition (iCVD). The LASO solid electrolyte offers high electrical resistance and chemical stability at the electrochemically active interface, while the pV4D4 solid electrolyte offers improvements in the mechanical integrity of the electrode. A hybrid film consisting of 5 nm LASO and 400 nm PV4D4 demonstrated a room temperature ionic conductivity of 3.4 x 10^{-7} S/cm, showing no significant increase in interfacial resistance. Integration with both 2D and 3D electrodes has shown substantial improvements in cycling and increased coulombic efficiency.

Current research on Li-ion batteries is directed at creating next generation electrode materials. One of the most viable 3D designs is through the use of nanowire electrodes, in which Si and Ge can offer much larger charge capacities (8444 A h L^{-1} for Li$_{15}$Si$_4$ and 7366 A h L^{-1} for Li$_{15}$Ge$_4$, respectively) than traditional carbon based anode materials, but suffer large volume expansion upon lithiation. Using an in-situ TEM electrochemical characterization technique, dynamic processes and structural changes are able to be observed during the lithiation/delithiation of a SiGe nanobattery in real time. Preliminary results show that ALD Li$_x$Al$_y$Si$_z$O-coated Si$_{0.4}$Ge$_{0.6}$ alloy nanowire demonstrates lithiation and delithiation with an intact solid state electrolyte layer with ~39% radial expansion observed upon lithiation.

9:20am **TF+EM-MoM4 Carbon Encapsulated CNT Micropillars for Silicon Lithium Ion Battery Electrodes**, *Kevin Laughlin, E. Laughlin, R. Fan, R.F. Davis, R.R. Vanfleet, J. Harb*, Brigham Young University
Here we present work on a hierarchical approach to structuring and encapsulating carbon nanotube (CNT) based carbon monoliths. Prior work has shown silicon has high gravimetric capacity, but increases by ~300%, and forms an unstable solid electrolyte interphase (SEI). High stability and lifetime operation requires nanostructuring of the silicon to alleviate stresses caused by the large expansion of the silicon upon Li alloying, and an encapsulation layer to restrict SEI build up. These CNT structures provide: porous scaffolding for silicon to expand to manage stress on multiple scales, a long conductive path for lithium transfer resulting in tall electrodes, and protection from unstable SEI formation. At high silicon loadings even nanoscale layers of silicon result in stresses large enough to cause mechanical damage to the electrode and encapsulation layer, resulting in lower capacity and cell lifetimes. By patterning the CNT scaffolding, we can contain the stresses caused by lithiation.

9:40am TF+EM-MoM5 Porous Oxide Shell on the Supported Gold Nanoparticles Synthesized via Polymer-Templated Atomic Layer Deposition, *Haoming Yan, X.Z. Yu, Q. Peng*, University of Alabama

Ultra small (≤ 5 nm) metal nanoparticles (USMNPs), especially Au, have attracted increasing attention due to their remarkable catalytic activity and selectivity in many important reactions. However, their catalytic properties are greatly affected by the poor thermal stability and the macro-molecular capping ligand (MCL) layer on their surfaces. Encapsulating the USMNPs with a porous oxide shell (pOXIDE) is a solution for both issues. So far, there has been limited success in generating the pOXIDE shell on the supported USMNP without significantly blocking its active sites. The objective of this work is to demonstrate the MCL layer templated atomic layer deposition (ALD) can be applied to synthesize the pOXIDE shell on the USMNPs to improve their thermal stability while keeping most of the surface active sites on USMNPs for the catalytic reaction.

10:00am TF+EM-MoM6 Three-Dimensional Solid State Batteries Grown Via Atomic Layer Deposition, *Alexander Pearse, T. Schmitt, D. Stewart, E. Sahadeo, K. Gregorczyk,* University of Maryland, College Park*, K. Gerasopoulos,* Johns Hopkins Applied Physics Lab*, G. Rubloff*, University of Maryland, College Park

Thin film solid state batteries have multiple attractive properties, including low interfacial impedance, exceptional cycling stability, and intrinsic safety, but have not seen significant implementation because their overall capacity is very low (on the order of 0.1 mAh/cm^2). This is a consequence of their growth by physical vapor deposition, which limits them to planar substrates. In this configuration, increasing areal capacity necessarily sacrifices rate performance due to slower ionic diffusion in thicker electrodes. Realizing practical energy or power densities in thin film SSBs will involve the development of entirely new fabrication processes in order to allow the integration of thin film SSBs with 3D substrates, such as micromachined silicon or conductive fabrics. In particular, 3D designs allow the decoupling of capacity and rate performance for area-normalized metrics.

We describe the development and synthesis of a solid state lithium-ion battery film stack grown entirely by atomic layer deposition (ALD), which allows us to successfully integrate solid state energy storage with 3D structures. The entire device is fabricated at temperatures at or below 250C, allowing for compatibility with a broad variety of substrates and processing environments. We utilize a simple electrochemical process for inserting free lithium ions into a crystalline cathode, avoiding the need to integrate lithiation into the ALD growth process itself. The solid electrolyte is a lithium polyphosphazene compound (a variant of LiPON) grown by a 2-precursor thermal process (Pearse et al. Chemistry of Materials 2017). The battery itself is comprised of a $LiV_2O_5 - Sn_xN_y$ couple, providing a reversible capacity of approximately 35 μAh/cm$_2$ μm$_{LVO}$ with an average discharge voltage of 2V. By growing these batteries into micromachined silicon structures with aspect ratios of up to 10, we are able to increase areal capacity by nearly one order of magnitude while simultaneously improving capacity retention at high rates- a type of scaling not possible for planar devices. We also discuss challenges associated with interface chemistry in the ALD growth environment and with patterning highly conformal films, and compare device performance to finite element electrochemical simulation.

10:40am TF+EM-MoM8 Systematic Investigation of Geometric Effects in Porous Electrodes for Energy Conversion Reactions, *Julien Bachmann*, University of Erlangen, Germany   **INVITED**

Inexpensive energy conversion devices necessitate novel strategies towards reducing the need for rare functional materials. One such strategy consists in accurately controlling the interface's geometry.

In our work, the pore walls of an anodic nanoporous template are coated with either galvanic deposition or atomic layer deposition (ALD) to obtain structured electrode surfaces that provide the experimentalist with a well-defined, tunable geometry. Indeed, the platform consists of a hexagonally ordered array of metallic or oxidic nanotubes of cylindrical shape, embedded in an inert matrix. The diameter of the tubes can be defined between 20 and 300 nm and their length between 0.5 and 100 μm, approximately. They can be utilized as a model system in which the electrode's specific surface area can be increased and its effect on the electrocatalytic current characterized systematically.

Diffusion-limited electrochemical transformations remain unaffected by changes in the length of the electrode's pores, whereas the steady-state galvanic current density observed for slow multielectron transformations increases linearly with the pore length. In particular, this approach enables us to achieve an increase of the electrochemical water oxidation turnover at neutral pH on iron oxide surfaces by three orders of magnitude. These results highlight a strategy for optimizing electrochemical energy transformation devices which could be generalized: the geometric tuning of catalytically mediocre but abundant and cost-effective material systems.

11:20am TF+EM-MoM10 Development of a Reduction-resistant Oxide Electrode for Dynamic Random Access Memory Capacitor, *CheolJin Cho, M.-S. Noh, W.C. Lee,* Korea Institute of Science and Technology, Republic of Korea, *C.H. An,* Seoul National University, Republic of Korea, *C.-Y. Kang,* Korea Institute of Science and Technology, Republic of Korea, *C.S. Hwang,* Seoul National University, Republic of Korea, *S.K. Kim*, Korea Institute of Science and Technology, Republic of Korea

Rutile phase TiO_2/RuO_2 structures have attracted great interests as a new material system for next-generation dynamic random access memories (DRAM) capacitors because of the high dielectric constant (> 80) of the rutile TiO_2. A conducting oxide electrode, RuO_2, enables the TiO_2 dielectric to be crystallized into a rutile phase at low temperatures (< 300 ºC). Since RuO_2 has a high work function, it is effective to suppress leakage current by Schottky emission which is a main conduction mechanism of TiO_2/RuO_2. However, the RuO_2 electrode is easily reduced during the post-annealing under forming gas atmosphere for trap passivation at the gate oxide/Si interface. Subsequently, the dissociated oxygen ions from RuO_2 cause problems such as the oxidation of W plug. The oxidation of W plug causes a fatal deterioration in device operation because the W plug acts as a path through which the charges of the capacitor move. Also, physical damage such as cracks will also occur when RuO_2(rutile) is reduced to Ru(hexagonal close-packed, HCP). For these reasons, we suggest a SnO_2-based electrode, which is a reduction-resistant material, as a new oxide electrode for DRAM capacitors. The reduction reaction of SnO_2 is thermodynamically more difficult than that of RuO_2. Also, a small amount of Ta ions is incorporated into the SnO_2 films to enhance the conductivity of the electrode. The resistivity of SnO_2 is reported to reach down to $10^{-4}\Omega\cdot$cm by Ta doping, which is sufficient for use as an electrode of DRAM capacitor. Furthermore, the Ta-doped SnO_2 films are well crystallized into a rutile phase, thereby leading to the formation of rutile TiO_2 at a low growth temperature (< 270 ºC). Therefore, we demonstrate that Ta-doped SnO_2 would be a promising candidate for the electrodes for next-generation DRAM capacitors.

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