ALD Applications
Room Hall 3D - Session AA1-MoA

Energy: Batteries and Energy Storage

Moderators: Christian Dussarat, Air Liquide Laboratories, **Jin-Seong Park**, Hanyang University

1:30pm **AA1-MoA-1 Enabling Fast Charging of Lithium-ion Batteries at Sub-Zero Temperatures with ALD coatings***, T. Cho, Y. Chen, D. Liao,* University of Michigan*; E. Kazyak,* University of Wisconsin*; D. Penley, **Neil P. Dasgupta**,* University of Michigan

Increasing the achievable charging rate of lithium-ion batteries (LIBs) is critical to the widespread commercialization of electric vehicles (EVs). However, it becomes increasingly challenge to charge batteries at low temperatures (< 5 °C), which is a major challenge facing adoption of EVs in cold climate

The primary factor limiting the ability of state-of-the-art LIBs to charge under both high-rate and low-temperature conditions is the propensity for Li metal to plate out on the graphite surface during charging.[1] The poor reversibility of Li metal in LIB electrolytes leads to rapid capacity fade, consumption of the electrolyte, and safety concerns. This problem is exacerbated in high-energy density cells with thicker electrodes, leading to energy-power tradeoffs.

To mitigate these effects, we have previously demonstrated that Li plating can be significantly suppressed during fast charging by implementing an atomic layer deposition (ALD) surface coating of a lithium borate-carbonate (LBCO) solid electrolyte directly onto calendered graphite anodes[2]. This ALD single-ion conductor has previously been shown to exhibit ionic conductivities above $2*10^{-6}$ S/cm and excellent electrochemical stability, including with Li metal.[3] In comparison to uncoated control electrodes, the LBCO a-SEI coating: 1) eliminates natural SEI formation during formation cycles, 2) decreases interphase resistance by >75% compared to that of the natural SEI, and 3) extends cycle life significantly under fast-charging conditions.

Building upon this demonstration of improved fast-charge ability with ALD coatings, in the current study, we demonstrate the ability of an artificial SEI layer deposited by ALD to also enable fast charging at sub-zero temperatures (down to -10 °C) while maintaining extreme fast charging rates (up to 6C) without Li plating[4]. This remarkable result is enabled by a synergistic combination of interfacial modification by ALD and fabrication of 3-D architected electrodes. These results demonstrate the power of decoupling interfacial and bulk mass transport effects under extreme charging temperatures, providing new fundamental insights into the factors that limit performance and result in cell degradation. In the future, the ability to fast-charge LIBs in cold environments will accelerate electrification of technologies in a broader range of geographic locations.

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3. E. Kazyak et al., *J. Mater. Chem. A* **6**, 19425 (2018)
4. T. H. Cho, Y. Chen, D. W. Liao, E. Kazyak, D. Penley, N. P. Dasgupta, *Submitted* (2024)

1:45pm **AA1-MoA-2 Atomic Layer Deposition of Lithium Borate and Borophosphate Thin Films for Lithium-ion Battery Applications***, **Tippi Verhelle**, A. Dhara, L. Henderick,* Ghent University, Belgium*; J. Meersschaut,* IMEC Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Lithium-ion batteries (LiBs) play a vital role in modern society, but challenges arise from unwanted side-reactions at the electrolyte/electrode interface. A promising solution to this issue involves the application of an ultrathin, protective coating on the electrode using atomic layer deposition (ALD). Previous studies highlight ALD's effectiveness in addressing such challenges, emphasizing thickness control and conformality [1]. Our research focuses on advancing this strategy by developing lithium borophosphate as a coating material for enhanced LiB performance.

In the work of Kazyak et al. [2], who used ALD to obtain a lithium borate-lithium carbonate intermixed material, the potential use of lithium borates (albeit with carbon inclusion) was evidenced. In this work, we aimed to achieve ALD of pure lithium borate films, which served as a starting point for new and optimized lithium borate mixtures towards even more controlled electrochemical properties. Our aim is to intermix this pure lithium borate with lithium phosphate, leveraging the latter's stability. Despite lithium phosphate's inherently lower ionic conductivity, namely 1.4 x 10^{-10} S cm^{-1} as deposited by ALD [3], studies using other deposition techniques have demonstrated that combining it with lithium borate effectively enhances the conductivity [4].

Our research introduced a new process for depositing lithium borate, utilizing lithium bis(trimethylsilyl)amide (LiHMDS), H_2O and trimethylborate (TMB). At 250°C, the process exhibited linear growth, with a growth per cycle of 0.04 nm, and saturation for every precursor step (Fig. 1). This process displayed a variation in composition as indicated by ERD (Fig. 2) and electrochemical properties at different deposition temperatures. With impedance spectroscopy (EIS), we calculated the conductivity of an 80 nm lithium borate thin film deposited at 250°C to be 1.60 ± 0.03x 10^{-7} S cm^{-1}at 30°C, with an activation energy of 0.58 ± 0.01 eV (Fig. 3).

Integrating this lithium borate with the well-known lithium phosphate process [5] was achieved through a supercycle approach. Varying the number of lithium phosphate subcycles relative to a constant number of lithium borate subcycles resulted in coatings with distinct electrochemical behavior. Our findings offer practical insights for tailoring LiB coatings with controlled electrochemical properties, contributing to advancements in battery technology.

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2:00pm **AA1-MoA-3 Fluorine-free ALD Process Produces Fluorine-rich Cathode Electrolyte Interphase for Lithium Batteries***, **Giulio D'Acunto**, S. Shuchi,* Department of Chemical Engineering, Stanford University*; Y. Cui,* Department of Materials Science and Engineering, Stanford University; Stanford Institute for Materials and Energy Sciences, SLAC National Accelerator Laboratory; Department of Energy Science and Engineering, Stanford University*; S. Bent,* Department of Chemical Engineering, Stanford University; Department of Energy Science and Engineering, Stanford University

The continuous evolution of lithium-ion and lithium-metal batteries is pivotal for meeting the growing demands of high-performance energy storage systems. Central to this advancement is the enhancement of the cathode-electrolyte interphase (CEI), a critical component in determining battery efficiency and safety. A fluorine-rich CEI is widely recognized for its role in enhancing Li^+ ionic conductivity and chemical stability. A fluorine-rich CEI is typically achieved by using fluorinated solvents, fluorinated additives, or an artificial SEI comprised of fluorinated materials. This research introduces an innovative approach to CEI improvement through the application of atomic layer deposition (ALD). Our design approach aims to utilize i) the high reactivity of the ALD precursors toward the existing cathode binder (polyvinylidene fluoride, PVDF), and ii) the surface acidity of the deposited thin film to induce more anion decomposition, further enhancing the fluorination of the CEI.

Leveraging the nanoscale precision and uniformity of ALD, we chose to develop a LiAlxOy coating on lithium-nickel-manganese-cobalt-oxide (NMC) cathodes. Li(HMDS) and TMA are used as metal precursors and water as a co-reactant. An M1-O-M2-O super-cycle, where M1 and M2 refer to the metal precursors, and O represents water, is used for the $LiAl_xO_y$. After exploring process parameters to enhance Li content and achieve saturation, the coated NMC cathode was characterized by angle-resolved X-ray photoelectron spectroscopy (ARXPS). We found evidence of Li-F species comprising nearly 50% of the total fluorine species, in contrast to less than 10% for the uncoated NMC cathode. The effectiveness of the fluorine-rich coating was then evaluated with electrochemical measurements, comparing the ALD-coated NMC to the bare NMC. The capacity retention of the coated cathode outperforms by almost a factor six that of the bare cathode, using a baseline carbonate-based electrolyte. Moreover, the characterization of the CEI after 50 cycles in the battery shows that i) the F-rich ALD coating is preserved during cycling, working as an artificial CEI, and ii) the native CEI overlayer atop the ALD layer is more fluorinated due to the surface acidity impact. This novel approach using ALD to achieve a fluorine-rich artificial CEI via a fluorine-free cathode coating process offers a more environmentally friendly approach compared to traditional methods.

2:15pm **AA1-MoA-4 Atomic Layer Deposition of Interface-Engineered $Li_4Ti_5O_{12}$: Toward High-Capacity 3D Thin-Film Batteries***, **Jan Speulmanns**, S. Bönhardt, M. Czernohorsky, W. Weinreich,* Fraunhofer Institute for Photonic Microsystems IPMS, Germany

Atomic layer deposition (ALD) of Li-compound thin films has aroused significant interest in recent years. Promising applications are Li-ion thin-film batteries (TFBs), protective particle coatings, and neuromorphic computing. Here, we evaluate $Li_4Ti_5O_{12}$ (LTO) fabricated by ALD for 3D solid-state TFBs to power upcoming autonomous sensor systems.

The simultaneous increase of power and energy density of 3D TFBs can be achieved by coating the battery layer stack over microstructured substrates. The required conformal, pinhole-free deposition and stoichiometric control of nanometer-thin films on highly structured surfaces are only accessible via ALD. However, direct ALD of Li-compound anodes remains challenging.

In previous studies, we developed a thermal three-step ALD process for Li-containing oxides on 200 mm Si wafers. Lithium-tert-butoxide (LTB) and lithium hexamethyldisilazide (LiHMDS) were proven as suitable precursors, forming spinel LTO with low impurities. The excellent electrochemical behavior of LTO with LiHMDS was linked to the film texture.

In this work, we optimize the LTO ALD process with LTB toward 3D TFBs and evaluate the electrochemical performance for the first time. A process with a saturated growth per cycle of 1.06 Å $cycle^{-1}$ for 7 s LTB pulses was developed. An ALD temperature window between 240 and 320 °C was identified. The effect of the substrate on the initial growth and crystallization behavior was investigated. The crystallization-inhibiting effect of the titanium nitride current collector is suppressed by introducing an AlO_x interlayer.

Planar LTO films with various thicknesses of up to 75 nm were manufactured by ALD, increasing the footprint capacity from 1.5 to 4.3 µAh cm^{-2}. However, the C-rate performance of thicker films is inferior due to the low conductivities of LTO. 50 nm films demonstrate the optimum energy and power density. A footprint capacity of 1.95 µAh cm^{-2}, corresponding to 65 % of the theoretical capacity, was achieved at 50 C.

Next, we evaluate ALD LTO films as 3D TFB anodes. The conformality of the ALD process was improved by extending the LTB pulse and purge times to 11 and 20 s. The purge time is the key factor enabling a step coverage of 70 % for holes with an aspect ratio of 10:1. 3D samples with an area-enhancement factor of 9 obtained a footprint capacity of 19.8 µAh cm^{-2} at 1 C. The large capacity increase by a factor of 6.75 compared to planar samples is according to the conformality. The power performance of 3D LTO samples at high C-rates will be discussed. The superior performance of ALD LTO is a key enabler for high-volume production of on-chip high-capacity 3D TFBs.

2:30pm **AA1-MoA-5 ALD for Advanced Lithionic Devices: Hybrid Ultrathin Solid-State Electrolytes***, **Ilyass GHANDARI**, N. GAUTHIER, S. POULET,* CEA-LETI, France*; M. BECHELANY,* CNRS, France*; M. BEDJAOUI,* CEA-LETI, France

Innovative micro-supercapacitors (MSCs) such as LiPON based MSCs are emerging to address the technological challenges faced at higher frequencies (>kHz),especially energy harvesting and storage, which requires efficient materials coupled with improved microfabrication techniques to unlock the full potential of such devices. In this way, conformal and self-limiting surface reactions enabled by Atomic Layer Deposition (ALD) give great advantages to form and optimize Lithium based thin films compatible with complex geometries. Here in, a multidisciplinary approach was conducted to develop the thermal ALD process, characterize the physico-chemical properties and evaluate the electrical performances of nano-hybrid Solid State Electrolytes (SSE).

The thermal ALD process for ultrathin LiPON films (<25nm) is realized using Li-Bistrimethylsilylamide (LiHMDS) and Diethylphosphoramidate (DEPA) precursors in a deposition temperature range 300-350°C. To further optimize LiPON's electrochemical performances, Trimethyl Aluminium (TMA) and H_2O were pulsed to incorporate Al_2O_3 in SSE films. Ellipsometry was used to calibrate the growth rate of LiPON-based films. The microstructure was analyzed by X-Ray Diffraction (XRD) to highlight the amorphous nature of the thin films, indicating that the Al_2O_3 incorporation preserves favorable amorphous structure, which is a key characteristic for achieving excellent electrochemical performances [1]. The XPS spectra show typical core peaks (Li_{1s}, P_{2p}, O_{1s}, N_{1s}, Al_{2p}) corresponding to different LiPON based samples. The analysis reveals that Al_2O_3 insertion seems to impact the nitrogen environment. From N1s spectra (Fig.1), the peaks present two main components located at 397 eV and 399 eV, attributed respectively to a divalent nitrogen state (N_d) and a trivalent nitrogen state (N_t) [1], whose proportion evolves as a function of Al_2O_3 incorporation. Thus, the concentration of divalent nitrogen becomes predominant over trivalent nitrogen, inducing an increase in the N_d/N_t fraction when more Al_2O_3 is introduced. This variation has frequently been reported as a major factor in improving Li-ion mobility [1]. The Electrochemical Impedance Spectroscopy (Fig.2) addresses the changes in Li-ion conductivity of the LiPON films upon addition of Al_2O_3 concentration.

This work provides a solid ALD approach with promising potential to optimize the electrical performances (ie Li^+mobility, areal capacitance etc) in ultrathin SSE, shedding light on the application of such hybrid microstructures in several Lithionic devices such as micro-supercapacitors, micro-batteries and transistors.

1:ACS Appl.Mater.Interfaces2016,8,11,7060–7069

2:45pm **AA1-MoA-6 Low Temperature ALD of Vanadium Sulfide (Ultra)thin Films for Nanotubular Supercapacitors***, **Raul Zazpe**, M. Sepulveda, J. Rodriguez-Pereira, L. Hromadko, M. Kurka, H. Sopha, J. Macak,* University of Pardubice, Czechia

Metal sulfides (MSs) are materials exhibiting a great variety of interesting inherent properties including semiconducting nature, high electrical conductivity and capacitance, (photo)catalytic capability, excellent redox reversibility and their abundance and low-cost.[1] Thus, MSs nanomaterials are a prospective alternative in multidisciplinary applications demonstrating a promising performance in energy conversion and energy storage devices[1] sensors,[2] photodetectors,[3] and biomedical applications[4] among others. Among the wide range of MSs, vanadium-based materials exhibit outstanding electrical conductivity and capacitance together with an excellent redox reversibility and electrochemical properties.[5] Vanadium is an abundant element that exhibits multiple oxidation states, which provides a rich and versatile chemical reactivity. Consequently, vanadium sulfides have been explored as promising materials as electrode material for supercapacitors (SCs).[6]

Herein, we present for the first time the synthesis of vanadium sulfide (VxSy) by Atomic Layer Deposition (ALD) based on the use of tetrakis(dimethylamino) vanadium (IV) and hydrogen sulfide.[7] The (ultra)thin films V_xS_y are synthesized in a wide range of temperatures (100 - 225 °C) and extensively characterized by different methods. The chemical composition of the V_xS_y (ultra)thin films reveals different vanadium oxidation states and sulfur-based species. Extensive X-ray photoelectron spectroscopy analysis studies the effect of different ALD parameters on the V_xS_y chemical composition. We further explore the electrochemical properties of ALD V_xS_y (ultra)thin films as electrode material for supercapacitors by coating TiO_2 nanotube layers (TNTs) with different numbers of V_xS_y ALD cycles at 100 °C. Long-term cycling tests reveal a gradual decline of electrochemical performance due to the progressive V_xS_y thin films dissolution under the experimental conditions. Nevertheless, V_xS_y coated TNTs exhibit significantly superior capacitance properties, as compared to the blank counterparts. The enhanced capacitance properties exhibited are derived from the presence of chemically stable and electrochemically active S-based species on the TNTs surface.

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3:00pm **AA1-MoA-7 Boosted Zn^{2+} Storage Performance of Hydrated V_2O_5 by Defect and Heterostructure***, V. Nguyen, J. Kim, **Seung-Mo Lee**,* Korea Institute of Machinery & Materials (KIMM), Republic of Korea

The inherent sluggish Zn^{2+}diffusion and poor electronic conductivity limit the ion intercalation/deintercalation process in aqueous Zn-ion batteries (ZIBs) using an oxide-based cathode. Here, we demonstrated that a heterostructure in the form of defective hydrated V_2O_5 embedded in the porous carbon textile (d-VOH@CT) could tackle these issues. To obtain the d-VOH@CT heterostructure, a V_2O_5 layer was deposited on waste cotton textiles using atomic layer deposition (ALD), followed by pyrolysis. The carbothermic reduction of V_2O_5 ($C + V_2O_5 \rightarrow C' + V_2O_3 + VC + CO/CO_2(g)$) coated on cotton textile transformed the cotton into the porous carbon textile covered with a hybrid VC/V_2O_3 layer. In the air, this VC/V_2O_3 layer was naturally oxidized to defective hydrated vanadium oxide (d-VOH) flakes embedded in the porous carbon textile (CT). The additional edges created by crystal defects significantly promoted facile Zn-ion adsorption and intercalation. Expanded interlayer spacing and reduced crystalline domain size kinetically facilitated fast Zn-ion diffusion in d-VOH flakes with shortened diffusion paths. Moreover, the heterostructure of d-VOH on the conductive carbon textile triggered rapid charge transfer, leading to high rate capability and structural stability. The ZIBs fabricated using the d-VOH@CT cathode delivered a preferable reversible capacity of 416 mA h g^{-1} at 0.1 A g^{-1}, an impressive energy density of 293 W h kg^{-1}, and a long cycle life. In addition, the d-VOH@CT heterostructure was able to be used as a freestanding cathode for a flexible ZIB with outstanding mechanical robustness and electrochemical stability.

3:15pm **AA1-MoA-8 High Throughput Atomic Layer Deposition of Niobium Oxide Thin Film for Lithium-ion Battery Application***, S. Kamimura, C. Dussarrat,* Air Liquide Laboratories, Japan*; **Nicolas Blasco,*** Air Liquide Advanced Materials, France

Surface modification of cathode active materials (CAMs) by atomic layer deposition (ALD) is known to improve the structural stability, ionic interfacial conductivity, and consequent charge-discharge characteristics of lithium-ion batteries (LiBs). The powder ALD technique has been shown to be highly effective in producing inorganic films, even on the particles of CAMs, with high conformality, uniformity and self-limiting growth, providing exceptional control over film thickness down to sub-nanometer level. Although the current powder ALD technique can successfully handle large amounts of nanoparticles for conformal coating with ALD, it requires a large amount of precursor for high surface area when working with fine particles, causing unique challenges for the ALD precursor. The dosage of the precursor/co-reactant is directly related to the surface area of the particles; the larger the area, the longer the exposure time required, resulting in a longer process time. Therefore, an ALD precursor that enables a high growth rate of inorganic thin films is in high demand.

We have conducted the synthesis screening of several types of organometallic niobium precursors for ALD and have successfully deposited an ALD Nb_2O_5 film using an organometallic precursor called Nautilus. This precursor showed a higher volatility & higher growth rate than tris(diethylamide)(tert-butylimido)niobium (TBTDEN). The Nb_2O_5 thin film growth on Si wafer was evaluated by QCM, XPS and ellipsometry measurements, and an outstanding GPC of 2 Å/cycle was determined at 225 ^oC, increasing with reactor temperature while maintaining excellent step coverage.

Powder ALD with Nautilus precursor was performed at 250 ^oCusing a fluidized bed reactor to achieve uniform Nb_2O_5thin film coating on CAMs. The TEM/EDS analysis shows that the entire surface of CAMs particles was uniformly covered with Nb_2O_5thin film with a thickness of ~1 nm even after 3 ALD cycles. The electrochemical performance measurements were conducted in R2032 coin-type cells (half cell). We clearly found that the Nb_2O_5thin film coating can suppress undesirable side reactions such as electrolyte decomposition on CAMs, and lead to the long-term cycle stability of discharge capacity. In the presentation, we will introduce the ALD characteristics of Nautilus and its LiB performance evaluation.

Author Index

Bold page numbers indicate presenter