ALD Applications
Room Van Rysselberghe - Session AA2-MoA

ALD for Energy Storage

Moderators: Ageeth Bol, University of Michigan, Ann Arbor, Philippe Vereecken, IMEC, Belgium

4:00pm AA2-MoA-11 Conversion Reactions and Redox Changes on the Surface of Lithium-Ion Battery Cathode Materials during Chemical Vapor Treatment for ALD, *P. Darapaneni, A. Mane, Z. Hood, Jeffrey Elam,* Argonne National Laboratory

Atomic layer deposition (ALD) has emerged as a promising technology for applying ultrathin protective coatings on lithium-ion battery (LIB) cathode surfaces to improve their cycling stability. While there have been numerous reports evaluating the electrochemical performance of these surface-modified cathode materials, the chemical changes induced on the surface of the cathode materials by the ALD coatings and the individual ALD precursors are not fully studied. We performed a systematic investigation to understand the interfacial changes of 12 different cathode materials upon coating with aluminum oxide (Al_2O_3) using trimethyl aluminum (TMA) and H_2O, and aluminum fluoride (AlF_3) using TMA and hydrogen fluoride pyridine (HFPy). We also explored the effects of the individual TMA and HFPy precursors on the cathode surfaces. The surface composition and microstructure of these cathode materials, which range from simple transition metal oxides (e.g., NiO and MnO) to complex multi-element cathode materials (e.g., $LiNi_xMn_{1-x-y}Co_yO_2$, NMC), were studied via X-ray photoelectron spectroscopy (XPS) and scanning transmission electron microscopy (STEM). The XPS measurements reveal that the transition metals in the cathode materials undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, XPS and STEM measurements show the conversion of surface carbonate species to the corresponding metal fluorides upon HF exposure. This conversion reaction is self-limiting but extends hundreds of nanometers below the surface in the case of Li_2CO_3. ALD and chemical vapor treatment provide new avenues to systematically control the interface of the cathode materials in LIBs that are not possible by conventional coating methods.

4:15pm AA2-MoA-12 Titanium Carboxylate MLD Hybrid Films as Protective Coatings for Lithium-Ion Batteries, *Sofie S. T. Vandenbroucke, L. Henderick,* Ghent University, Belgium*; L. De Taeye,* IMEC, Belgium*; J. Li,* Ghent University, Belgium*; K. Jans, P. Vereecken,* IMEC, Belgium*; J. Dendooven, C. Detavernier,* Ghent University, Belgium

Li-ion battery cathodes age due to phenomena as transition metal dissolution, electrolyte oxidation and volume expansion. [Vetter J., et al. (2005) *J. power sources*] A protective coating can be applied to the cathode's surface to avoid direct contact with the electrolyte. Many studies have shown the protective effect of conformal and pinhole-free ALD films. However, inorganic films are rigid and may crack upon volume expansion of the cathode. [Ban C., et al. (2016) *Adv. Mat. Int.]* MLD offers the same deposition controllability as ALD but can be used to deposit hybrid films that are more flexible to accommodate potential volume expansions. In this work, titanium carboxylate thin films are deposited using tetrakis(dimethylamido)titanium (TDMAT) and various dicarboxylic acid precursors: oxalic acid, malonic acid, succinic acid, glutaric acid and 3,6-dioxaoctanedioic acid (Fig 1). The latter containing two ethylene oxide units per molecule, potentially increasing the Li-ion conductivity. [Xue Z., et al. (2015) *J. Mat. Chem. A*]

The growth of the titanium carboxylate thin films is studied using in situ ellipsometry at a substrate temperature of 100 and 160 °C. Only the TDMAT/oxalic acid process displays good saturation behavior, while a parasitic CVD component is present during the TDMAT pulse for the other processes (Fig 1). FTIR and XPS confirm the successful deposition of titanium carboxylate films. The films are found to be stable in air up to 50 days in contrast to many metalcone MLD films. In addition, FTIR, XRR and XRF measurements show that the films remain intact upon immersion into the liquid electrolyte used for electrochemical characterization (1 M $LiClO_4$ in propylene carbonate).

The electrochemical properties of 5 nm films grown with TDMAT/oxalic acid, TDMAT/3,6-dioxaoctanedioic acid and TDMAT/glycerol (titanicone film [Van de Kerckhove K., et al. (2016)*Dalton Trans.*]), respectively, are compared on top of three ideal electrode systems: anatase TiO_2, TiN and $LiMnO_2$ (LMO). The titanium carboxylate films have little to no effect on the

Li-ion kinetics of the TiO_2 electrode system. This is in contrast to the titanicone film displaying a detrimental effect on the kinetics. All films effectively suppress electrolyte oxidation when exposing the TiN electrode system to elevated potentials (Fig 2). On the LMO electrode an activation step is necessary for all films, after which a good Li-ion mobility through the titanium carboxylate films is observed without the severe irreversible reactions detected for the titanicone film. Overall, the titanium carboxylate films seem promising candidates as flexible coatings to protect Li-ion battery cathodes.

4:30pm AA2-MoA-13 Surface Coating and Grain Boundary Engineering of NMC811 Materials for Next-Generation Li-Ion Batteries, *Zahra Ahaliabadeh, V. Miikkulainen,* Aalto University, Finland*; M. Mäntymäki,* University of Helsinki, Finland*; T. Kallio,* Aalto University, Finland

Nickel-rich layered metal oxide $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811) is one of the most promising cathode materials owing to its high energy density. Therefore, these cathode materials have a prime interest for the electric vehicle battery manufacturers to build next-generation lithium-ion batteries. However, NMC811 suffers from several irreversible parasitic reactions and interfacial/structural instability that lead to severe capacity fading and impedance buildup during prolonged cycling. Thin surface protection films coated on the electrode material are feasible and effective solutions to solve these challenges. It can mitigate degradative chemomechanical reactions at the electrode–electrolyte interphase, which helps to increase cycling stability. However, most of the coatings including metal oxide may impede the diffusion of lithium ions, and therefore, limit the performance of the cathode material. Thus, the physical and chemical properties of the coating materials are effectual factors in providing optimized protection for the electrode materials. In our research, we worked on the deposition of Li-containing metal oxide layers with different thicknesses through atomic layer deposition method, on the surface of NMC811. Lithium titanate, was coated on the NMC811 electrode and found to be effective in the elimination of surface impurities and reducing the capacity loss. Characterization analysis such as Scanning electron microscopy (SEM-EDS) and Transmission Electron Microscopy (TEM) results confirmed the diffusion of the coating in to the NMC grain boundaries which helped to stabilize the structure, as evidenced by providing longer lifetime with an 87% capacity retention after 100 cycles. Besides the characterization and electrochemical analysis, *in-situ* dilatometry and *in-situ* XRD analysis showed irreversible volume change for NMC811 bare while it was mostly reversible for the coated ones during the cycling. The results revealed that the dilation behavior of the electrode, resulting in crack formation and particle degradation, has been significantly suppressed for the coated samples. The ability of the coatings to mitigate the electrode degradation mechanisms, provides insight into a method to enhance the performance of Ni-rich positive electrode materials. To enhance the electrochemical performance of NMC811 under high-voltage ranges, the addition of organic molecule to the coating is suggested. Such a hybrid coating layer can combine the functions of promoting Li^+ ion transport, as well as enhancing the electrical conductivity due to the coating structural properties. This new coating is under examination and its results will be demonstrated later.

4:45pm AA2-MoA-14 Hybrid Inorganic/Organic Polycarbonate Track-Etched Membranes With Tunable Pore Size and Surface Functionality for Redox Flow Batteries, *Rajesh Pathak,* Applied Materials Division, Argonne National Laboratory*; X. Fang,* Indiana University–Purdue University Indianapolis*; R. Shevate, V. Rozyyev, A. Mane,* Applied Materials Division, Argonne National Laboratory*; X. Wei,* Indiana University–Purdue University Indianapolis*; Z. Xia,* Argonne Center for Molecular Engineering, Argonne National Laboratory*; L. Zhang,* Chemical Science and Engineering Division, Argonne National Laboratory*; S. Babinec,* Argonne Collaborative Center for Energy Storage Science (ACCESS), Argonne National Laboratory*; S. Darling,* Argonne Center for Molecular Engineering, Argonne National Laboratory*; J. Elam,* Applied Materials Division, Argonne National Laboratory
Abstract

Redox flow batteries (RFBs) hold great promise for the stationary storage of renewable energy from solar and wind power because they combine high safety with low cost, and because they decouple energy density and power density through the physical separation of redox-active species in liquid solutions. Despite these positive attributes, the high cost of existing RFBs limits their widescale deployment in the electric power grid. Significant cost reduction is possible if new technologies for the manufacture of low-cost, highly selective ion transport membranes can be developed. In this study, we explore isoporous polycarbonate track-etched

membranes (PCTEs) modified by sequential infiltration synthesis (SIS) and atomic layer deposition (ALD) to tune the pore size and pore surface chemistry as a platform for developing low-cost, high-performance RFB membranes. We perform a systematic study of Al_2O_3 SIS and ALD in PCTE to establish the range of conditions that yield precise control over the membrane pore size.Next, we functionalize the pore wall surfaces with a variety of ALD metal oxide coatings to tune the surface charge and hydrophilicity.Finally, we evaluate the membrane properties and performance in aqueous organic redox flow batteries with (ferrocenylmethyl)trimethylammonium chloride (FcNCl)/methyl viologen (MV) in noncorrosive neutral sodium chloride supporting electrolyte to establish structure-function-property relationships.We anticipate that this work will provide a pathway to developing low-cost inorganic/organic ion transport membranes for RFB applications.

Keywords: atomic layer deposition; sequential infiltration synthesis; neutral aqueous organic redox flow battery; selective ion-transport; high-permeability; (ferrocenylmethyl)trimethylammonium chloride; methyl viologen

5:00pm AA2-MoA-15 TiO₂ ALD Thin Films Characterization for SiC Capacitor, *R. César, José Diniz,* University of Campinas - UNICAMP, Brazil

Silicon carbide (SiC) has become a very promising material in the microelectronics industry due to its properties. In this way, being widely used in the development of MOSFET, diodes and MOS capacitors, mainly used in high temperature and high power applications. However, the SiC interface presents higher charge density that limits the use of SiO2 as gate dielectric. Dielectric options such as aluminum oxide and titanium oxide (TiO2) have been studied for passivation of interfacial defects. TiO2 stands out due to its qualities such as: high dielectric constant, chemically and thermally stable. Thus, this work presents the study carried out with thin films (15, 25 and 35 nm) of TiO2 deposited by ALD to be used as gate dielectric in SiC capacitors. The structural characterization consists of ellipsometry and spectroscopy Raman. The electrical characterization was performed using capacitance by voltage (CxV) and current by voltage (IxV) using silicon MOS capacitors. Through the ellipsometry technique it was possible to obtain the refractive index (η) values of the TiO2 films, which ranged from 2.06 ~ 2.32. The refractive index of the stoichiometric TiO2 is 2.41. This result indicates that these films have a higher concentration of oxygen than titanium. Raman spectroscopy showed that all films have a rutile crystalline structure, identified by the letter R in Figure 1 (Appendix), and the presence of the anatase crystal structure, identified by the letter A in Figure 1 (Appendix). From CxV and IxV curve, it was possible to it was possible to extract the data that compose the 1, 2 and 3 tables (Appendix). It can be seen from all tables that the VFB values are decreasing in all three cases, indicating the relationship of VFB with the device geometry. Another very important parameter presented by the three thicknesses is the absence of hysteresis. It is very common for TiO2 films deposited by ALD to present hysteresis values greater than 10 mV. Hysteresis is related to charge trapped at the dielectric/semiconductor interface, generated during the device manufacturing process. Therefore, it can be assumed that the capacitors developed in this work have low trapped load values. The 25 and 35 nm thick oxide capacitors presented dielectric constant values with a decreasing behavior, and 15 nm thick oxide capacitor showed an ascending behavior. However, the films showed dielectric constant values ranging from 11 ~ 56. Thus, it can be concluded that these TiO2 films deposited by ALD have rutile and anatase crystal structure, high dielectric constant and low charge density and leakage current density values, being ideal for use in SiC capacitors.

5:15pm AA2-MoA-16 ALD Can Enable Competitive, U.S.-Sourced Graphite Production, *Arrelaine Dameron, D. Higgs, B. Hughes,* Forge Nano

U.S. demand for LIBs is projected to grow to >400GWh by 2030 but U.S. battery manufacturing is currently dependent on foreign (primarily China) supply of graphite materials. The coated spherical purified graphite (CSPG) production processes are energy intensive and derived from petroleum. The spherical graphite is purified by leaching, caustic and thermal treatments to remove metal impurities and is then coated by a liquid phase tar (derived from petroleum processing) that fills surface pores and reduces the surface area. The tar itself is also fractionated and purified through size separation and solvent extraction to produce the ideal precursor feedstock. The coated particles are then dried and baked at >1200 °C for days in an inert-gas oven.

FN has developed ALD coatings to disrupt the pitch coating process. FN has previously shown ALD coatings can improve CSPG graphite. Recently, FN has <u>also</u> demonstrated that ALD can improve uncoated graphite to a higher performance (capacity and rate tolerance) and longer lifetime than pitch coated graphite with all the added advantages of economically and environmentally improved process to generate a competitive domestic supply of battery grade graphite. This process is applied to the purified and spheronized graphite and then can be directly packaged or cast into anode materials. Drying, thermal treatment and further physical processing are not required. This low vacuum or atmospheric pressure process can we applied continuously at low temperature (<150 °C instead of 1200 °C) greatly increasing the throughput of the process while decreasing the carbon footprint significantly. This nano-coating process can replace traditional tar pitch coating processes for spherical graphite used in the anode of LIB. Combining up incoming US manufacture of high purity graphite and FN's nano-coatings will enable domestic production of low-cost anode-grade graphite materials for lithium-ion batteries and simplify supply chain logistics, while reducing national security risk. Establishing a completely U.S. battery supply chain, using disruptive U.S.-based technology, will deliver both material supply resilience and improved production rates. Use of ALD-coated spherical graphite will also deliver a lower cost and safer battery for U.S. consumption. ALD-coated spherical graphite is a drop-in replacement for foreign sourced materials and seamlessly integrated into standard Lithium-ion battery production methods. This talk will demonstrate the various benefits of ALD coatings on graphite for LIB, scaling these processes to production scale, and compare ALD graphite relative to the incumbent CSPG technology.

5:30pm AA2-MoA-17 Plasma-Enhanced Atomic Layer Deposition of Nickel and Cobalt Phosphate for Lithium Ion Batteries, *Lowie Henderick, R. Blomme, J. Keukelier, M. Minjauw,* Ghent University, Belgium*; J. Meersschaut,* IMEC, Belgium*; J. Dendooven,* Ghent University, Belgium*; P. Vereecken,* IMEC, Belgium*; C. Detavernier,* Ghent University, Belgium

Since the introduction of a lithium iron phosphate electrode in Li-ion batteries (LIB's), metal phosphates have become increasingly important. Apart from LIB's, metal phosphates have also been proven promising towards e.g. electrocatalytic water splitting, biocompatible coatings, etc., which is why research on their deposition also becomes increasingly important. Atomic Layer Deposition (ALD) has emerged as a deposition technique with unique nanotailoring capabilities, making the combination of both research fields gain a lot of interest. Although it has been challenging to find a suitable phosphate precursor, the use of trimethyl phosphate (TMP) has allowed for the deposition of a variety of metal phosphates (Henderick et al. (2022) *Appl. Phys. Rev.*). Unfortunately, its poor reactivity limits the deposition of metal phosphates with e.g. a high phosphorus-to-metal (P/M) ratio. Interestingly, the use of a TMP plasma (PE-ALD) allowed for the deposition of other, more connected (more P-O-P bonds, figure 1), metal phosphates.

In this work, a novel PE-ALD process was developed for the deposition of nickel phosphate ($NiPO_x$), which was not yet available through ALD. The process is based on an earlier report where a TMP plasma (TMP*) is combined with an oxygen plasma (O_2*) and a metal precursor. Using nickelocene as the metal precursor, saturated growth of an amorphous $NiPO_x$ was observed at a substrate temperature of 300°C, with a growth per cycle of 0.2 nm/cycle (figure 2). Using XPS, the nickel is thought to be in the 2+ oxidation state, while the position of the oxygen and phosphorus peak agree with the formation of a phosphate-like material.

As $NiPO_x$ is currently of interest as a LIB electrode, the material was also electrochemically characterised together with cobalt phosphate using a previously reported ALD process (Rongé et al. (2019) *Nanoscale Adv.*). Both materials showed electrochemical activity (figure 3), although at a lower voltage window than what is supposed to be achievable with these phosphates. This relatively low operating voltage is expected to originate from the 2+ oxidation state of nickel (and cobalt) in the as-deposited material, while a 3+ oxidation state would be needed for the high energy redox reactions to take place. Both materials did show a good rate performance with a reasonable cycle life.

We hope that the novel PE-ALD process developed in this work can help to extent the knowledge on ALD of metal phosphates. We also hope that it sparks interest towards further fine-tuning such processes to optimise the layers towards their respective application (e.g. LIB's and/or other potential applications).

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