ALD Applications
Room Grand Ballroom E-G - Session AA2-TuA

ALD for Batteries II

Moderator: Yong Qin, Institute of Coal Chemistry, Chinese Academy of Sciences

4:00pm **AA2-TuA-11 Tunable Electrical Properties of Lithium Fluoride Thin Films using Different Fluorine Sources***, **Devika Choudhury**, A Mane, J Elam,* Argonne National Laboratory

Considering that it has one of the largest optical bandgaps, lithium fluoride is probably the most popular material of choice for ultraviolet coatings today, as compared to other metal fluorides like MgF_2 and AlF_3. The low refractive index of 1.39 (at 580nm) also makes it useful as a window material in the UV-region of electromagnetic radiation.[1] Other utilities of LiF include thermoluminescent detector layers for X-rays and extreme UV sensor applications, electron injection layers in LED or photovoltaics etc.[2] Apart from optical applications, LiF may be useful as a protective coating on the cathodes of Li-ion batteries due to its chemical stability and wide electrochemical window. In this regard, LiF can be mixed with other metal fluorides to improve the lithium-ion conductivity while maintaining the chemical stability. Lithium ion conductivities of order 10^{-6} S/cm at room temperature have been reported for Li_3AlF_6 and Li_2NiF_4.[3]

LiF thin films grown by atomic layer deposition have been reported earlier using lithium tert-butoxide and HF-pyridine resulting in a room temperature ionic conductivity of 10^{-14} S/cm.[4] In this work we explore the possibility of growing LiF films with alternate sources of fluorine, WF_6 and MoF_6. *In-situ* quartz crystal microbalance and fourier transform infrared spectroscopy studies are carried out to obtain the growth characteristics of the films. Compositional analysis is obtained from XPS measurements. Impedance spectroscopy measurements are performed to evaluate the effect of LiF concentration in mixed metal fluoride coatings.

References:

1. Miia Matymaki et al., Chem. Mater. 2013, 25, 1656.

2. John Hennessy et al., Inorganics 2018, 6, 46.

3. T. Oi et al., Mater. Res. Bull. 1981, 16, 1281.

4:15pm **AA2-TuA-12 The Role of Al_2O_3 ALD Precursor Chemistry on the Electrochemical Performance of Lithium Ion Battery Cathode Mmaterials***, **Donghyeon Kang**, A Mane, J Elam,* Argonne National Laboratory*; R Warburton, J Greeley,* Purdue University

Al_2O_3 coatings prepared by atomic layer deposition (ALD) using trimethyl aluminum (TMA) and H_2O on lithium metal oxide cathode surfaces have been shown to enhance the performance of lithium ion batteries. However, the effects depend on the choice of cathode material. For example, 1-2 TMA/H_2O cycles on lithium cobalt oxide (LCO) dramatically improves cyclability and slightly decreases capacity [1]. In contrast, the same treatment on lithium manganese oxide (LMO) improves capacity but has little effect on cyclability [2]. Furthermore, the TMA surface reactions on LMO are unusual in that they do not involve hydroxyls, ethane is released, and the Mn undergoes redox chemistry. Density functional theory (DFT) calculations reveal that this unique mechanism is driven by the large free energy changes upon methyl loss from TMA [2]. This leads us to speculate that the surface reactions and subsequent electrochemistry might also depend on the choice of Al precursor. To evaluate this hypothesis, we are exploring a range of aluminum precursors including trimethyl aluminum (TMA), tris(dimethylamido) aluminum (Al-TDMA), aluminum trichloride ($AlCl_3$), dimethyl aluminum isopropoxide (DMAI), and aluminum triisopropoxide (ATIP) on a variety of cathode materials such as LCO, LMO, and nickel manganese cobalt (NMC) materials. Our initial results suggest a correlation between cation reduction on the cathode surface and the relative Lewis acidity of the Al precursor ligands. We will elaborate on these findings using results from XPS measurements, DFT calculations, and coin cell cycling studies.

[1] Y. S. Jung et. al., *J. Electrochem. Soc.*​**157** (1) A75-A81, (2010).

[2] L. Chen et. al., *Chem*​**4** 2418-2435 (2018).

4:30pm **AA2-TuA-13 Spatial Atomic Layer Deposition of Hybrid Nanolaminates for High Capacity Li-ion Battery Electrodes***, E Balder, L Haverkate, M Tulodziecki, F van den Bruele, S Unnikrishnan,* ***Paul Poodt****,* TNO/Holst Center, Netherlands

Lithium-ion batteries have become the dominant battery technology in many applications. For future applications, there are still several challenges that need further development, including increasing the energy- and power density, reducing charging time, increasing the lifetime and improving the safety of operation. Solutions to these challenges can be found in combinations of new battery architectures, high performance materials and manufacturing methods.

ALD could be one of these new manufacturing methods, because of its unique characteristics in terms of film quality, uniformity and step coverage. For that reason, ALD is being explored for a wide variety of functional layers inside battery devices. One main drawback of ALD is its low deposition rate, limiting throughput and thereby leading to high manufacturing costs. Atmospheric pressure Spatial ALD could be a solution to this challenge, as it combines all the benefits of ALD with high deposition rates and scalability to large areas. Spatial ALD technology has already been developed for high performance applications in e.g. photovoltaics, roll-to-roll SALD for barrier foils and large-area SALD for OLED displays. This technology can potentially also be used as future manufacturing method of next generation solid state (3D) lithium ion batteries.

A material that is receiving considerable attention as an electrode for lithium-ion batteries is TiO_2, since it offers a potentially cheap, environmentally friendly and stable alternative to the current electrode materials. However, due to its low electronic conductivity and poor Li-ion conductivity it has a poor rate performance. The rate performance of TiO_2 films can be increased by decreasing the thickness, which comes at a cost of capacity. Nanolaminates of TiO_2 films can be used to maximize both the capacity and rate performance, where a stack of a number of thin TiO2 films will have a higher capacity than a monolithic film with the equivalent thickness. We have used Spatial ALD to make a hybrid nanolaminate film composed of thin TiO_2 layers separated by decoupling layers made by Spatial MLD of aminophenol-based titanicones. These decoupling layers have both a sufficient electrical conductivity and ionic conductivity in order for Li ions to penetrate in the underlying TiO_2 layers. When tested in a coin cell configuration, these nanolaminate electrodes demonstrate a 2-3 higher capacity than the reference, bulk $TiO\text{-}_2$ electrodes of the same thickness, a high Coulombic efficiency and a good cycling stability.

These results demonstrate the potential of nano-scale engineered high performance electrodes made by high throughput Spatial ALD.

4:45pm **AA2-TuA-14 Lithium Organic Thin Films for Various Battery Components***, **Juho Heiska**, M Karppinen,* Aalto University, Finland

The field of energy storage is constantly evolving and facing new challenges. The next-generation batteries should be cheap, constitute of abundant elements only, and show electrochemical performances at least on par with the current state-of-the-art lithium-ion batteries. One of the promising new material families is the organic electrode materials; they are composed of light elements and thus possess high gravimetric capacities. Organic electrode materials do however suffer from low electronic conductivity and solubility issues when applied with a liquid electrolyte. Coating the organic materials with a thin passivation or solid-electrolyte layer is an effective way to suppress the dissolution without dramatically affecting the electrochemical properties. An attractive way to deposit these layers in a controlled manner is the atomic/molecular layer deposition (ALD/MLD) method. When organic electrodes are deposited with ALD/MLD the redox mechanisms are easy to experiment on since the system works as such without any conducting carbon or binder making it a simple model system. The deposition of solid electrolytes or protective coatings is also a highly feasible application for ALD/MLD.

In this research, a new ALD/MLD processes were developed for promising organic electrode materials and novel Li-organic coatings. The experimented molecules are related on the known electrode material lithium terephthalate with additional functional groups which alter the electrochemical properties. Since the bulk electrode composition is not standard in literature the comparison of the materials is difficult and prone to error. When the thin films of lithium-2-aminoterephthalate and lithium-2,5-dihydroxyterephtalate (Li_2DHTP) are compared with lithium terephthalate (Li_2TP) the direct comparison of electrochemical performance is possible. We find that both of the films do decrease the redox voltage as expected but also the flat discharge plateau of Li_2TP is lost. In addition, the rate capability and the cycling life of the films were negatively affected. We propose that the functional groups that donate electron density to the π-conjugated system are causing π-π repulsion between adjacent molecules. In addition, it was found hydroxyl groups of Li_2DHTP are lithiated at low potentials vs. Li^+/Li. Also, a novel lithium ethylene glycol ALD/MLD process was developed showing promising properties as a coating material for lithium-ion batteries. This and previous studies demonstrates the feasibility of this approach for developing better batteries and battery materials and highlights the potential of ALD/MLD technique for actual battery applications.

5:00pm **AA2-TuA-15 ALD Infiltration of $LiCoO_2$ for High Rate Lithium Ion Batteries**, ***Ian Povey****, M Modreanu, S O'Brien,* Tyndall National Institute, Ireland*; T Teranishi, Y Yoshikawa, M Yoneda, A Kishimoto,* Okayama University, Japan

Atomic layer deposition (ALD) was selected to deposit Al_2O_3 on cathode active material, $LiCoO_2$, to create a protective barrier layer [1], supress the high potential phase transition and thus reduce the subsequent Co dissolution [2]. However, surprisingly in this study it was found that it also resulted in the reduction of the charge transfer resistance at the cathode-electrolyte interface, thus enhancing the performance of the battery and not just its robustness. Energy-dispersive X-ray spectroscopy, in conjunction with transmission electron microscopy, shows that a discrete Al_2O_3 shell was not formed under the selected growth conditions and that the Al diffused into the bulk $LiCoO_2$ [3]. The resulting active oxide material, which was significantly thicker than the nominally Al_2O_3 ALD growth rate would predict, is proposed to be of the form $LiCoO_2$: Al with amorphous and crystalline regions depending on the Al content. Cells fabricated from the modified electrodes were found to have good cycling stability and discharge capacities of ~110 $mAhg^{-1}$ and ~35 $mAhg^{-1}$ at 50C and 100C respectively. Here we discuss the reasoning behind these observations and through a series of electrode treatments prior to ALD tune the behaviour.

[1] I.D. Scott, Y.S. Jung, A.S. Cavanagh, Y. Yan, A.C. Dillon, S.M. George, S-H. Lee, Nano Lett. 11 (2011) 414-418

[2] J.H. Woo, J.J. Travis, S.M. George, S-H. Lee, J. Electrochem. Soc. 162 (2014) A344-A349

[3] T. Teranishi, Y. Yoshikawa, M. Yoneda, A. Kishimoto, J. Halpin, S. O'Brien, M. Modreanu, I. M. Povey, ACS Appl. Energy Mater. 1 (2018), 3277-3282

5:15pm **AA2-TuA-16 ALD Al_2O_3 and MoS_2 Coated TiO_2 Nanotube Layers as Anodes for Lithium Ion Batteries**, *H Sopha,* University of Pardubice, Czech Republic*; A Tesfaye,* Ecole Nationale Supérieure des Mines de Saint-Etienne, France*; R Zazpe,* University of Pardubice, Czech Republic*; T Djenizian,* Ecole Nationale Supérieure des Mines de Saint-Etienne, France*;* ***Jan Macak****,* University of Pardubice, Czech Republic

The miniaturization of Lithium ion batteries (LIBs) as a power source to drive small devices such as smartcards, medical implants, sensors, radio-frequency identification tags etc. has been continuously developed to meet the market requirements of portable applications.[1] In this direction, 3D microbatteries have been considered to satisfy the requirements of these portable devices. Anodic TiO_2 nanotube layers (TNTs) have been recently explored as anodes for LIBs due to their high surface area, low volume expansion, short diffusion lengths for Li^+ ion transport and good capacity retention even at faster kinetics.[2,3]

Recently, various coatings produced by Atomic Layer Deposition (ALD) on electrode materials have been explored extensively in LIBs. For example, Al_2O_3 and TiO_2 coatings act as a protective layer for the suppression of the solid electrolyte interphase (SEI) in various electrode materials.[4,5] But their influence on increasing the electronic conductivity of the electrode material has not been explored in details. In addition, it is also possible to synthesize using ALD the main electrode materials, such as oxides[6] and sulphides.[7] However, high surfacearea and sufficiently conducting support would be beneficial for these ALD derived materials to support an excellent performance of the batteries. The door for various one-dimensional nanomaterials, such as TNTs, is therefore open

In this presentation, we will show ALD synthesis of Al_2O_3[8] and MoS_2[9] coatings on TNTs as new electrode material for lithium-ion batteries. We show an influence of different coating thicknesses on the battery performance, in particular on the charging and discharging capacity.

References

1) B.L. Ellis, P. Knauth, T. Djenizian, Adv. Mater. 26 (2014) 3368-3397.

2) G. F. Ortiz et al., Chem. Mater. 21 (2009), 63–67.

3) T. Djenizian et al., J. Mater. Chem. 21 (2011) 9925-9937.

4) Y. S. Jung et al., Adv. Mater. 22 (2010) 2172−2176.

5) E. M. Lotfabad et al., Phys.Chem. Chem. Phys., 2013, 15, 13646

6) M. Y. Timmermans et al., J. Electrochem. Soci., 164 (2017) D954-D963.

7) D. K. Nandi et al., Electrochim. Acta 146 (2014) 706–713.

8) H. Sopha et al., ACS Omega 2 (2017) 2749-2756.

9) H. Sopha et al., ACS Applied Energy Materials, submitted.

Author Index

Bold page numbers indicate presenter