Thursday Afternoon, November 10, 2022

Surface Science Division
Room 319 - Session SS+AS+SE-ThA

ALD and CVD Surface Chemistry

Moderators: Melissa Hines, Cornell University, **Dario Stacchiola**, Brookhaven National Laboratory

2:20pm SS+AS+SE-ThA-1 ALD Surface Chemistry on Lithium-Ion Battery Cathodes, *Jeffrey Elam,* Argonne National Laboratory   **INVITED**
Next-generation energy storage devices demand superb control over interfaces. Atomic layer deposition (ALD) is a powerful strategy for controlling interfacial properties. ALD coatings can suppress undesirable electrochemical reactions between lithium-ion battery (LIB) cathode surfaces and the organic liquid electrolyte and improve LIB cycling stability. While numerous reports have evaluated the electrochemical performance of ALD treated 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. This presentation highlights our recent work investigating the surface chemistry of ALD on LIB cathode surfaces. We find that the nucleation and growth of Al_2O_3 ALD on$LiMn_2O_4$ (LMO) is much different compared to conventional surfaces such as hydroxylated SiO_2. For instance, LMO does not have surface hydroxyls under typical ALD conditions. During initial Al_2O_3 ALD cycles, trimethyl aluminum reacts with Mn-O bonds and reduces surface Mn ions generating C_2H_6. Al_2O_3 ALD on LMO is highly precursor-dependent and the degree of surface Mn reduction is strongly influenced by the Lewis acidity of the precursor ligands. In addition, the Al_2O_3 ALD growth per cycle (GPC) on LMO varies by 30x among 5 Al_2O_3 ALD precursors that exhibit essentially the same GPC on SiO_2. We next examined the surface chemistry for Al_2O_3 and AlF_3 ALD on 12 different cathode surfaces ranging 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). We found that the Ni, Mn, and Co transition metals in the cathode undergo selective oxidation/reduction depending upon the nature of the precursor, the coating, and the cathode material. Furthermore, our measurements revealed 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.

3:00pm SS+AS+SE-ThA-3 Role of Temperature, Pressure and Surface Oxygen Migration in the Initial Atomic Layer Deposition of HfO₂ on Anatase TiO₂(101), *G. D'Acunto, R. Jones,* Lund University, Sweden*; L. Pérez Ramírez,* Synchrotron Soleil, France*; P. Shayesteh, E. Kokkonen, F. Rehman,* Lund University, Sweden*; F. Lim, F. Bournel, J. Gallet,* Sorbonne Université, France*; R. Timm, **Joachim Schnadt**,* Lund University, Sweden
Atomic layer deposition (ALD) has become one of the prime methods for deposition of ultrathin films with atomic-scale precision [1,2]. Yet, for many ALD processes the underlying surface chemistry or aspects of it remain unclarified [3,4]. Experimental methods that allow the real-time monitoring of the ALD surface chemistry, i.e. time-resolved methods that can be applied during an ongoing ALD process, can provide much deepened insight into the ALD surface chemistry. One such method is time-resolved ambient pressure x-ray photoelectron spectroscopy (APXPS), which is an excellent match to ALD since it easily can be used in standard ALD pressure conditions of up to around 1 mbar. Here, we have applied APXPS to the study of the surface chemistry of the initial full cycle of HfO_2 ALD on $TiO_2(101)$ from tetrakis(dimethylamido) hafnium (TDAMHf) and water precursors at both high (500 K) and low (300 K) surface temperature as well as high (~10^{-1} mbar) and low (~10^{-6} mbar) pressure.

Generally, we find that the initial ALD process on $TiO_2(101)$ is characterised by an absence of surface hydroxyls, which implies that the reaction cannot proceed via the ligand-exchange mechanism standardly proposed for oxide ALD from amido complexes and water. Instead, dissociative adsorption and subsequent hydrogen insertion reactions take place during the first metal half-cycle, which lead to the formation of a number of different surface species, including a dimethyl ammonium ion and an imine. Their formation requires either a bimolecular reaction pathway or an active role of the $TiO_2(101)$ surface as an oxygen supplier. Both pathways are viable and may compete with each other. Oxygen transport is evident from the formation of HfO_2 during the very first half-cycle and a concomitant reduction of the

TiO_2 support already. The water half-cycle then allows hydroxyl formation, but only at sufficiently higher water pressure. In this case, a transition towards a ligand exchange reaction mechanism is possible, which, however, is hindered if the water pressure is too low.

Our study highlights how chemical models for transition metal oxide ALD from amido complexes and water need to be extended, by consideration of hydroxyl-free surfaces, oxygen transport and bimolecular reactions paths, and how time-resolved *in situ* studies can help understand how deposition parameters affect the growth of HfO_2.

[1] Miikkulainen, V.; Leskelä, M.; Ritala, M.; Puurunen, R. L. *J. Appl. Phys.* 2013, **113**, 021301

[2] Johnson, R. W.; Hultqvist, A.; Bent, S. F. *Materials Today* 2014, **17**, 236

[3] Zaera, F. *Coord. Chem. Rev.* 2013, **257**, 3177

[4] Richey, N. E.; De Paula, C.; Bent, S. F. *J. Chem. Phys.* 2020, **152**, 1

3:20pm SS+AS+SE-ThA-4 ALD of Well-Defined Mixed-Oxide and Metal-Oxide Catalytic Interfaces, *Francisco Zaera,* University of California - Riverside
As the chemistry of solids is in most instances determined by the nature of their surfaces, control over the nature of surface sites during preparation is critical to the design of materials for specific applications. This is a difficult task, especially when complex multicomponent atomic ensembles are required. In this presentation we illustrate how atomic layer deposition (ALD) may be used to prepare such sites. We will describe the development of prototypical surface sites comprised of mixtures of silica supports (mainly well-structured mesoporous materials such as SBA-15), titania thin films, and gold nanoparticles, as that combination has proven to offer some unique and useful surface chemistry for low-temperature catalysis. The materials resulting from the use of ALD approach have been characterized using a surface-science approach, relying on the use of adsorption-desorption isotherms and well-defined mesoporous structures together with electron microscopy and a variety of spectroscopic techniques, including IR, NMR, XPS, EPR, and Visible-UV absorption. They showed some unique redox properties, and were tested for the promotion of low-temperature oxidation and selective hydrogenation reactions. Time permitted, other mixed-oxide interfaces, in particular silica-alumina, will be introduced as well.

3:40pm SS+AS+SE-ThA-5 Mechanistic studies on Catalytically Activated ALD of Fe₂O₃ on Pt, *Andreas Werbrouck,* Stanford University, Belgium*; J. Schneider, S. Nathan, A. Rothman, S. Bent,* Stanford University
Atomic layer deposition (ALD) of Fe2O3 is well-studied process. Fe2O3 has numerous applications, for example in catalysis or as a ferroelectric material. While many Fe2O3 ALD processes have been reported, almost all of those use an iron precursor in combination with strong oxidizers such as H2O2, O3, or O2 plasma. Recently, ALD of Fe2O3 on Pt substrates has been demonstrated using just O2 gas as the co-reactant, with tert-butyl ferrocene (TBF) as the metal precursor [1]. The process was area selective, with no growth occurring on other substrate materials (SiO2, Al2O3, Au); hence, it is hypothesized that the Pt substrate creates reactive oxygen species in situ, effectively catalyzing the reaction to grow Fe2O3. Intriguingly, the activation continues after the Pt substrate has been completely covered by Fe2O3. The continued growth is attributed to the formation of a sub-surface oxygen reservoir.

In this work, we further investigate this process, with a focus on the underlying oxygen activation and transport mechanisms. In situ ellipsometry was used to study the growth characteristics and x-ray diffraction confirmed the Fe2O3 crystal structure. X-ray photoelectron spectroscopy results show a clear correlation between the amount of deposited Fe2O3 and the Pt surface coverage. To study the kinetics and mechanistic steps of the process, quadrupole mass spectrometry (QMS) was employed. H2O (m/z 18) CO (m/z 28, which is also N2) and CO2 (m/z 44) are observed as reaction products when Pt is present, indicating a combustion-like mechanism. Furthermore, as expected, the kinetics of the reservoir change as the film grows thicker; this behavior is confirmed by the QMS measurements.

Finally, a simple 1D diffusion model was developed to describe the sub-surface oxygen reservoir process (fig. 1). Given the partial pressure of O2, the model captures adsorption, transport and desorption of the oxygen in the layer before (O2) and after (O*) activation. The Pt surface coverage is parametrized too. The model yields observable outputs such as the amount of desorbing species and reaction products, but also parameters which are harder to access experimentally, such as the activation energies and kinetic constants and concentrations of the different species in the layer.

Comparison of the model results with experimental data should help provide deeper insight into the mechanism of catalytically activated ALD.

[1] Singh, Joseph A., et al. "Area-selective atomic layer deposition of metal oxides on noble metals through catalytic oxygen activation." Chemistry of Materials 30.3 (2018): 663-670.

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