



MSC GRADUATION PROJECT  
*Atomic Layer Deposition of Li-Based  
Materials for Battery Applications*

**Graduation Project**

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This thesis is public.

This thesis was made in accordance with the TU/e Code of Scientific Conduct for the Master thesis.

## Abstract

Increasing the energy density of Li-ion batteries (LIBs) is an important factor in the electrification of transport to enable longer ranges. A possible strategy to increase the energy density of LIBs is to increase the cut-off voltage. At high voltages degradation phenomena at the cathode-electrolyte interface (CEI) become a problem. Cathode model systems may provide insights into the formation of CEI layers and other parasitic reactions. Atomic layer deposition (ALD) has proven to be a valuable tool for interface control, where the ALD of Li-containing materials becomes increasingly relevant for the fabrication of battery components. Among the researchers at the Applied Physics department that work on Li-containing materials the focus lies on lithium nickel oxide (LNO) cathode materials. For their synthesis we adopt lithium-bis(trimethylsilyl)amide (LiHMDS) as Li-source. Using LiHMDS as Li precursor can result in the incorporation of Si in the film due to the presence of silyl groups. In order to control the dual-source behaviour the understanding of the LiHMDS ALD process reaction mechanisms is required. X-ray photoelectron spectroscopy (XPS) and *in situ* SE revealed that O<sub>2</sub> plasma as co-reactant leads to Si incorporation and linear growth, whereas the thermal ALD process resulted in Si-free films and high, non-surface limited growth. Time-resolved quadrupole mass spectrometry (QMS) measurements were taken during both ALD processes to elucidate the influence of the co-reactant on the reaction mechanism. We monitored relevant mass-to-charge ratios during full and half ALD cycles, as well as the reactor pressure, to ensure that the observed signals can be attributed to specific moments during the ALD cycle. The QMS measurements revealed that the incorporation of Si in the plasma-enhanced ALD process stems from the redeposition of combustion products of physisorbed ligands during the plasma step. This shows that the choice of co-reactant controls the dual-source behaviour of LiHMDS. The addition of a H<sub>2</sub> plasma step after the O<sub>2</sub> plasma also resulted in Si-free films by etching the previously incorporated Si. We found that applying this two step plasma approach in a supercycle process, with bis(N,N-di-tert-butylacetamidinato)nickel(II) (Ni(O<sup>t</sup>Bu–MeAMD)<sub>2</sub>) as Ni precursor for the deposition of LNO, still leads to the incorporation of Si in the film. Thus, an ALD process for a novel, Si-free Li precursor (*Lider*) was developed. Using a supercycle approach between *Lider* and the Ni precursor *Alanis*, Si-free LNO films with varying chemical compositions were deposited, as confirmed by XPS. LNO films with a Li/Ni atomic ratio close to 1, which is the desired LiNiO<sub>2</sub> stoichiometry, were obtained. X-ray diffraction (XRD) showed that the pristine LNO films were amorphous and annealing resulted in the formation of NiO rock-salt structures. Further research is needed to obtain LNO thin films with the desired layered-oxide structure. The insights gained in this work may help in the development of (1) LiHMDS-based ALD processes and (2) ALD processes for the deposition of Si-free LNO films for LIB applications.