Abstract ALD/ALE 2024

Title: Understanding the dual-source behavior of LiHMDS for Si-free Li-containing films

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The electrochemical stability of interfaces is key to long-lasting and safe Li-ion batteries. To study these interface processes, ALD can deliver thin film model systems of electrodes. For example, the behavior of Ni-rich $LiNi_xMn_yCo_{1-x-y}O_2$ cathodes can be understood by investigating $LiNiO_2$ thin films due to the similar electrochemical properties. Moreover, the control that ALD provides over film composition and crystal orientation allows to study how those material properties influence the interface stability. To grow $LiNiO_2$ by ALD, lithium hexamethyldisilazide (LiHMDS) is preferred over the widely-used LiO^tBu because of its lower melting point of 70°C, but the presence of silyl groups can result in the undesired incorporation of Si. Previous work proposes that Si is incorporated during both precursor and O_2 plasma steps in the ALD cycle [1]. However, processes in which the LiHMDS dose is followed by a H_2O pulse can yield Si-free films [2,3], indicating that the co-reactant plays a major role in the Si incorporation.

To shed light on the reaction mechanisms of LiHMDS and the two co-reactants, we carry out *in-situ* growth studies by spectroscopic ellipsometry and mass spectrometry (QMS) [4]. The O_2 plasma process shows linear growth and the film contains 16 at.% Si according to XPS, but the H_2O process results in bulk-driven growth and Si-free films. QMS shows that the difference between the processes lies in the reaction products during the co-reactant step: H_2O removes the HMDS ligands of physisorbed LiHMDS via a proton exchange reaction, whereas the O_2 plasma combusts HMDS. The redeposition of Si-containing combustion products during the plasma step is presumably the origin of the dual-source behavior of LiHMDS.

We also include a H_2 plasma step following the O_2 plasma step, with the hypothesis that H radicals can etch the incorporated Si. This process exhibits bulk-driven growth and the grown films are, as expected, Si-free and have a Li_2O composition. QMS confirms the release of SiH_x-species during the H_2 plasma step. Interestingly, the growth behavior and film composition remain the same when the order of the O_2 and H_2 plasmas is reversed. The QMS results in this case indicate that H_2 plasma removes the HMDS ligands and thereby prevents the Si incorporation in the subsequent O_2 plasma step.

Overall, this work shows that the co-reactant controls the reaction mechanism, and therefore the dual-source behavior, of LiHMDS. These insights can aid the fabrication of Si-free $LiNiO_2$ films.

[1] Werbrouck et al., J. Phys. Chem. C, 2020, 124

[2] Østreng et al., RSC Adv., 2012, 2

[3] Østreng et al., J. Mater. Chem. C, 2013, 1

[4] Pieters et al., to be submitted

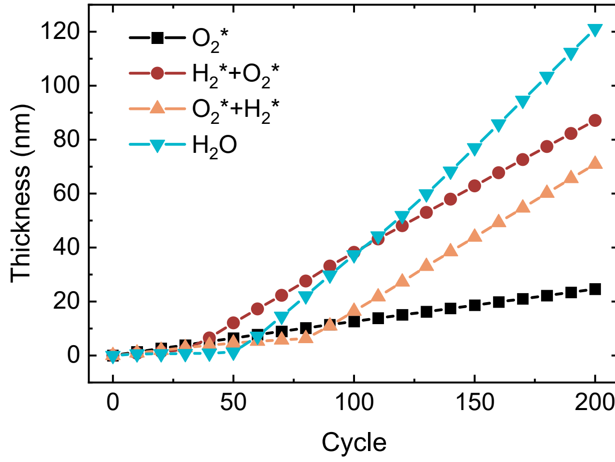

*Figure 1 Film thickness as a function of number of cycles for ALD processes based on LiHMDS with different co-reactants. The symbol * refers to plasma as co-reactant.*

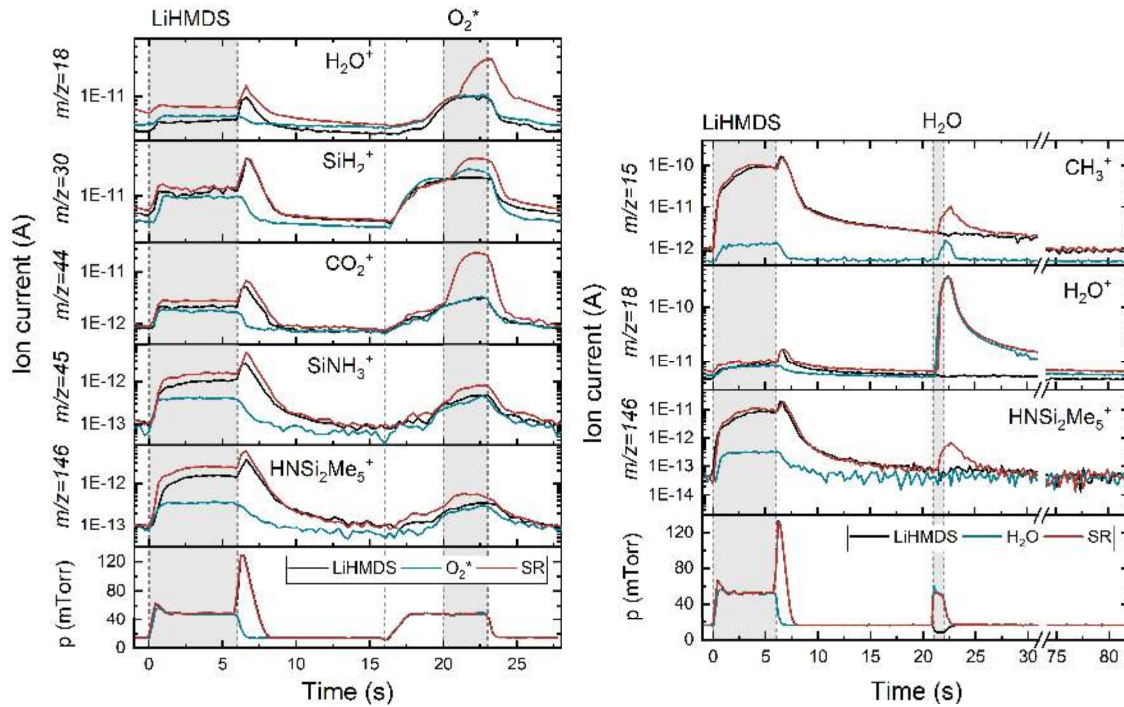

Figure 2 – Time-resolved quadrupole mass spectrometry (QMS) data of relevant m/z values for the LiHMDS+O_2 and LiHMDS+H_2O processes. The standard ALD recipe (SR) is compared to the recipes without the co-reactant (LiHMDS) and without the precursor (O_2* or H_2O). The pressure in the reactor is monitored to identify pressure-related features in the QMS data.*

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