Plasma-Enhanced Atomic Layer Deposition of Lithium Nickel Oxide Thin Film Model Systems

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The main bottleneck in the development of the next generation of Li-ion batteries with higher energy densities, as demanded for long-range electrical mobility, is the lack of understanding and control of the reactions at the electrode-electrolyte interfaces. Reactions at the cathode side cause rapid capacity loss during cycling and represent a major issue for batteries with high-voltage cathodes, which are crucial in reaching the required energy densities. Promising candidates for use in next generation of batteries are Ni-rich $Li(Ni_{1-x-y}Mn_xCo_y)O_2$ (NMC) cathodes, which show high capacity, high potential, and contribute to address the geopolitical issue of decreasing the Co content in the cathode. Ni-rich NMCs exhibit similar electrochemical properties as pure $LiNiO_2$ and therefore $LiNiO_2$ thin films can be used as model systems to gain fundamental understanding of the interfacial processes that hinder the large-scale implementation of Ni-rich NMCs. Atomic layer deposition (ALD) is a suitable technique to fabricate these model systems, as it gives precise control over film thickness, uniformity, chemical composition, and crystal orientation.

Previous work on $LiNiO_2$ by ALD is not extensively reported in literature. Moreover, films grown by an ALD supercycle process, in which two ALD subcycles are alternated, suffered from a low Ni at.% and a large C content because of precursor ligand residues, and films fabricated using a complex multilayered approach showed severe Si contamination from the Li precursor [1]. In this contribution we report on ALD lithium nickel oxide (LNO) thin films with stoichiometries close to $LiNiO_2$ and low level of contaminants.

The ALD process is based on lithium hexamethyldisilazide (LiHMDS) and nickel bis(*N*,*N*'-di-*tert*-butylacetamidinate) (Ni(^{t}Bu-MeAMD)$_2$) as precursors and O_2 plasma as co-reactant. 1 ALD cycle of Li_2O is combined with x cycles of NiO using a supercycle approach. In this contribution we explore the relation between the Ni/Li cycle ratio x and material properties of the LNO films.

The growth of the LNO films is monitored by means of in-situ spectroscopic ellipsometry. The ellipsometric data of films with a high Ni/Li cycle ratio are fitted with a general oscillator model used for NiO films, while a Cauchy model was adopted in case of a low Ni/Li cycle ratio and Li_2O films. The growth per supercycle (GPSC) of LNO shows an intermixing effect, as it does not follow the linear trend calculated from the growth per cycle (GPC) values of the individual Li_2O and NiO ALD processes, which are 1.0 Å/cycle and 0.34 Å/cycle respectively.

XPS surface measurements confirm that the Ni/Li atomic ratio is tuned from 0 to 10 as function of the Ni/Li cycle ratio x, and show that the LNO films contain low levels of Si and N contamination (below 4% and 2% resp.). A shift of the main peak in the Ni $2p^{3/2}$ spectrum to higher binding energies indicates a shift in oxidation state from Ni^{2+} to Ni^{3+} as x decreases [2]. According to surface measurements, the LNO film with $x = 5$ shows a stoichiometry close to $LiNiO_2$, but depth profile measurements indicate that the Ni at.% is significantly higher in the bulk than on the surface of the films, most certainly attributed to the formation of a Li_2CO_3 surface layer upon air exposure. Li_2CO_3 is also present in the bulk of the LNO films, but the bulk C at.% stays below 4%.

These results show that we can use ALD to fabricate a high-voltage cathode model system, which we plan to characterize in-situ and post-mortem in combination with both liquid and solid electrolytes to study the cathode-electrolyte interface.

[1] Maximov et al., Energies, **13** (2020) 2345

[2] Fu et al., Applied Surface Science **441** (2018) 1048

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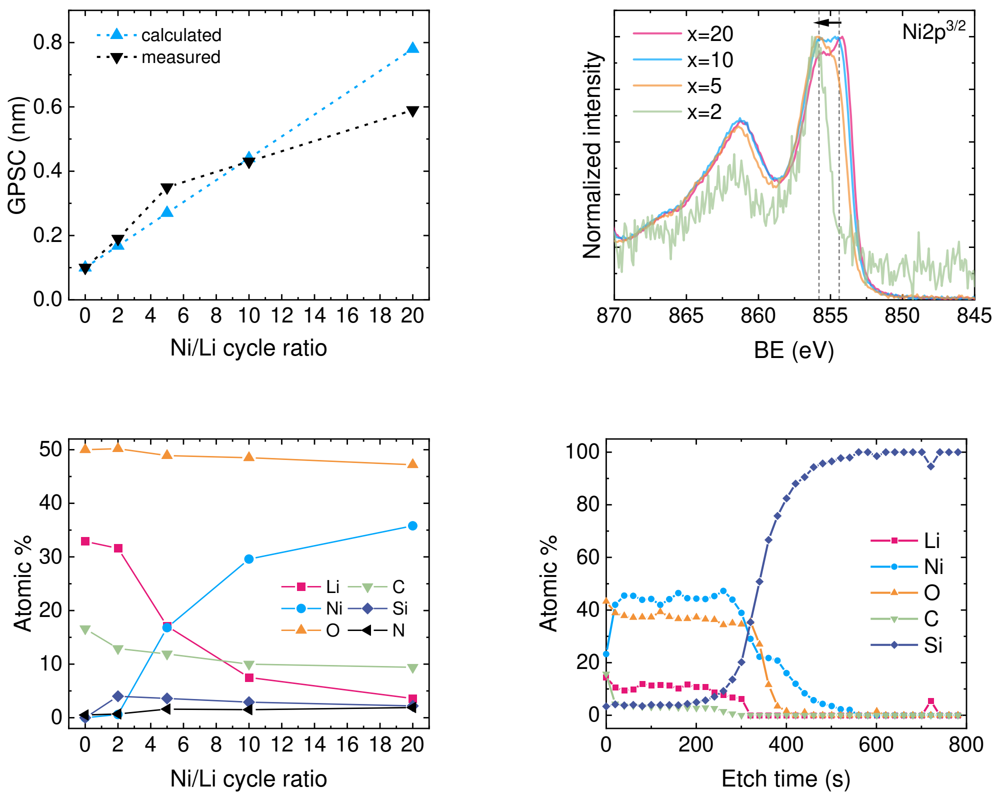

(a) The GPSC of LNO ALD process shows an intermixing effect when comparing the experimental results with the expected GPSC based on the two processes (b) Ni 2p XPS spectrum for different cycle ratios x. A shift to higher binding energies is observed with decreasing x, indicating a shift from Ni^{2+} to Ni^{3+}. (c) XPS surface measurements of LNO films show low levels of contaminants and a Ni/Li atomic ratio varying with the Ni/Li cycle ratio. (d) Depth profile of LNO with $x = 5$ shows an increased Ni at.% and a low C at.% in the bulk of the film.