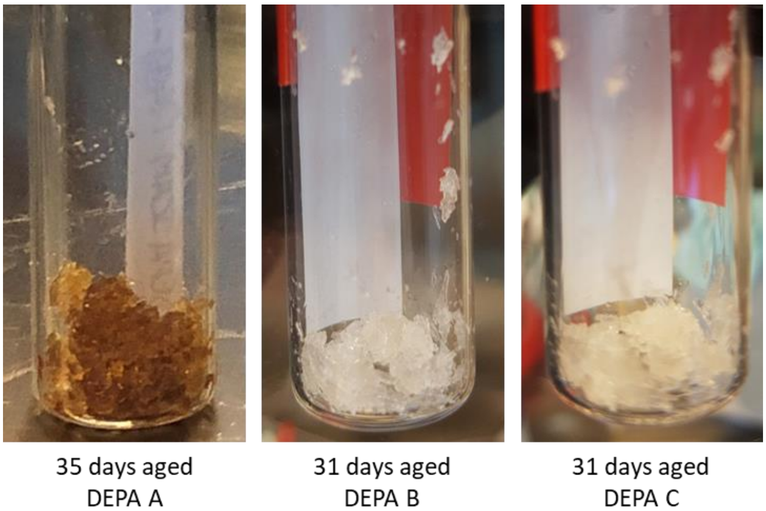
Supplemental information for: "Study of the chemical stability of precursors used for ALD of lithium-containing films by structural and thermal analyses" Nicolas Massoni et al., abstract submitted for a poster (AF8).

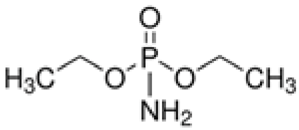
Preliminary remark: This work is a follow up of the ALD/ALE 2025 talk #AA2-WeA-12. In this document, you will find new data collected after ALD/ALE2025. They support our intermediate conclusions shown in 2025. Some of these new data were submitted for a regular publication to Chemistry of Materials (revised manuscript under review, Editor: Professor Han-Bo-Ram Lee).

The main objective of this study is to provide an understanding of the LiPON film growth to stabilize the actual process. While conventional ALD research often focuses on modifying the ligand of a precursor and conducting standard characterization, our work takes a different approach. We specifically investigated the short-term chemical stability of one of the usual commercial LiPON precursors, *i.e.* the diethylphosphoramidate (DEPA). The other precursor (lithium hexamethyldisilazide) was found to be chemically stable over time.

It was already found that DEPA was stable within 14 days, before starting to degrade by losing nitrogen. By means of calorimetry done between –80 to 100°C, unexpected impurities were detected in the as-supplied DEPA, which melted at –7°C. Those impurities might be responsible for the degradation of DEPA product. It was neither possible to refine commercial DEPA nor synthetizing lab-made DEPA. To slow down the degradation process, the tank temperature was lowered from 90°C to 80°C. However, saturation was not reached at 80°C. It was decided to try alternative DEPA suppliers. So, three different DEPA suppliers, denoted A, B and C were compared, with DEPA A being used since the beginning of the study.

As a first comparison test, the ageing of DEPA A, B and C was done in a closed ALD tank at 90°C during 30 days. No LiPON depositions were done. As expected, the DEPA A has degraded, turned brown and agglomerated (Figure 1). Surprisingly, the DEPA B and C remained white.





Theoretical DEPA structure

Figure 1. Pictures of aged DEPA A, B and C

As shown in Figure 2, the FTIR spectra of the as-supplied and aged DEPA samples have confirmed that the NH_x group is impacted by ageing for DEPA A only, as indicated by an asterisk. For suppliers B and C, the FTIR spectra are superimposed, indicating that ageing had no impact on their structure.

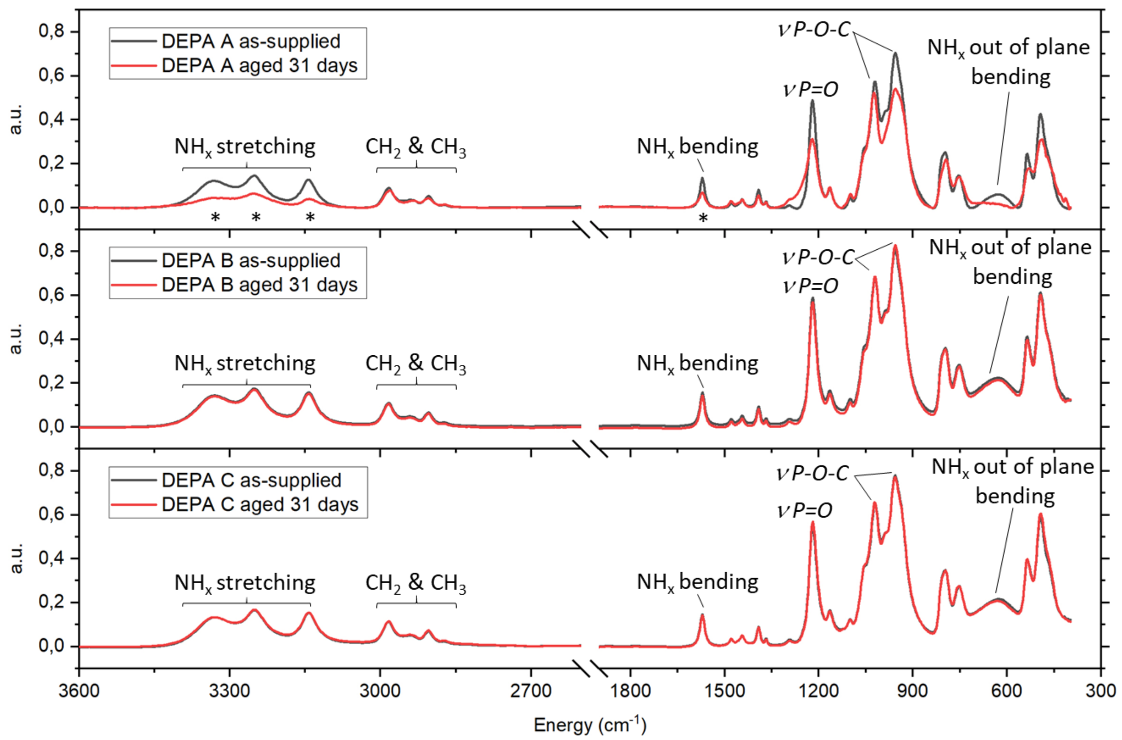


Figure 2. FTIR spectra of as-supplied and aged DEPA A, B and C

The impact of DEPA ageing on the LiPON layer is exhibited by Figure 3. The ionic conductivity of LiPON is about 1.3×10^{-8} $S.cm^{-1}$ just after the renewal of DEPA and remain quite stable until 14 days of ageing. After 36 and 70 days, it decreased to 4×10^{-9} $S.cm^{-1}$. DEPA is likely responsible for ionic conductivity degradation

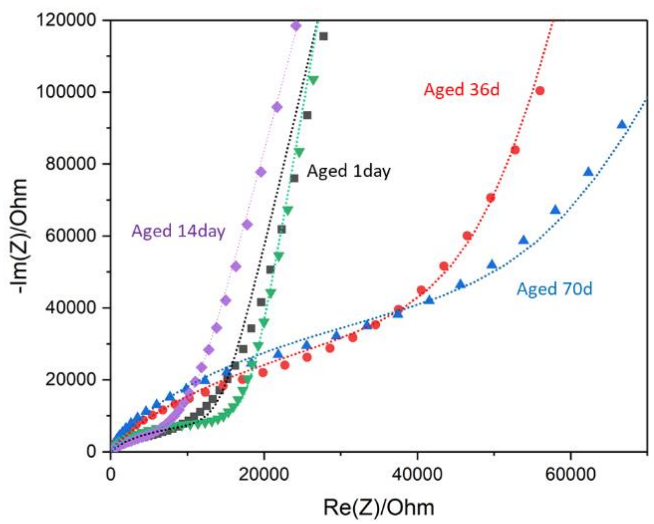


Figure 3. LiPON conductivity change with DEPA ageing, from supplier A

Several experiments are currently underway so that we can present the complete set of characterizations at ALD/ALE 2026.:

- ^{31}P and ^{1}H NMR data of DEPA to compare as-supplied and aged structures
- DSC of as-supplied DEPA A, B and C to reveal any impurities
- The LiPON conductivity evolution with DEPA B and C (same figure as Figure 3). A stable ionic conductivity is expected.

This study provides insight into the impact of precursor aging on LiPON film properties, such as GPC, stoichiometry, and conductivity.