Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Nanoscale Li, Na, and K Ion-Conducting Phosphazenes by Atomic Layer Deposition

R. Blake Nuwayhid[1], Daniela Fontecha[1], Alexander C. Kozen[1], Sang Bok Lee[2], Gary W. Rubloff[2], and Keith E. Gregorczyk*[1]

[1]Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742

[2]Department of Chemistry, University of Maryland, College Park, MD 20742

*Corresponding author: kgregorc@umd.edu

Experimental Procedures:

LiPON, NaPON, and KPON were synthesized by ALD, characterized by XPS, and electrochemically tested with EIS as described in our previous publications.[1, 2] The experimental procedures for the *in-operando* quadrupole mass spectrometry (QMS) study on LiPON is described below. A MKS Vision 2000-C QMS was connected directly to the Fiji ALD reactor ($<10^{-6}$ Torr) through a 1.33'' OD CF conflat flange. A picture of the ALD-coupled QMS in our lab is displayed in Figure S1a. The QMS valve configuration is shown in Figure S1b, which possess two inlets, V1 for low pressure sampling (<10 mTorr) and V2 for high pressure process sampling (up to 20 Torr). The use of the needle valve allowed us to maintain a low pressure in the QMS and use the higher sensitivity V1. The pressure in the QMS was maintained at 10^{-6} Torr through the turbo pump on the QMS. The system is equipped with a faraday cup detector and electron multiplier detector, in which the electron multiplier detector was used with an ionization energy of 70 eV.

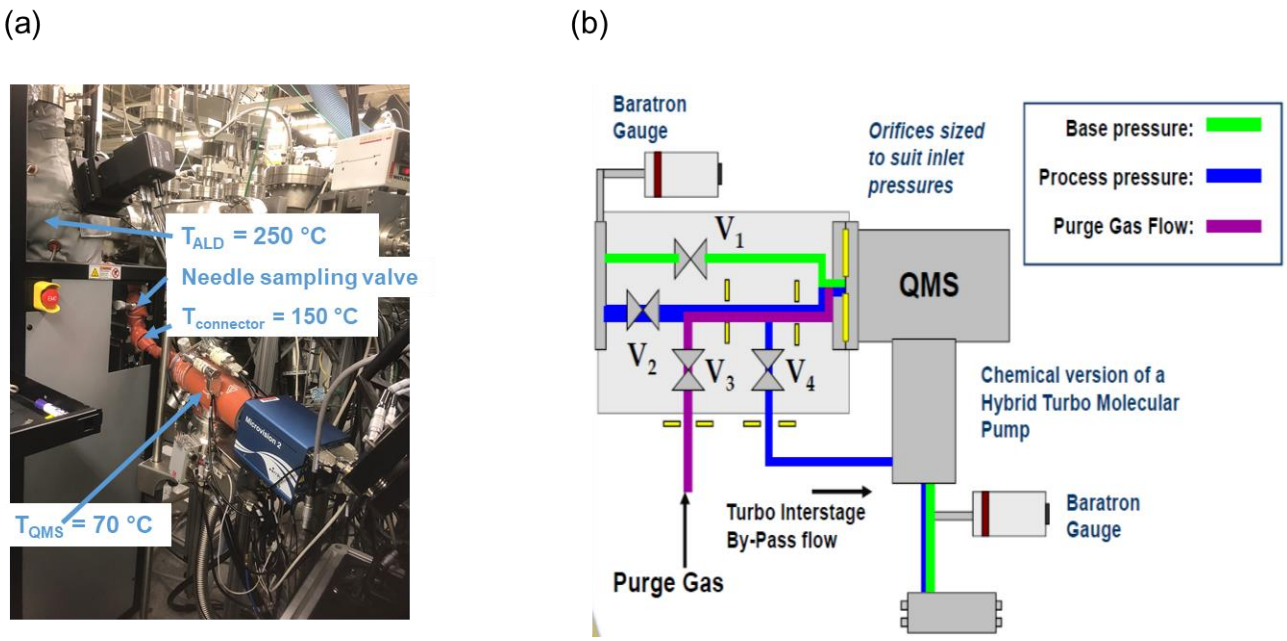

Figure S1. (a) Picture of ALD coupled QMS setup. (b) Valve configuration of QMS system.

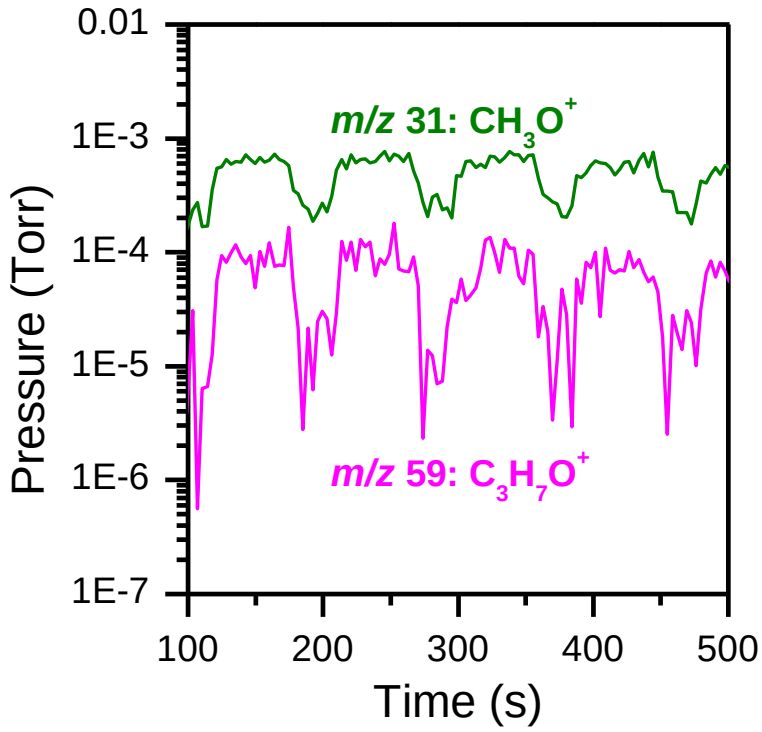

Figure S2. Time-resolved mass spectra of repitive 60 s LiO^tBu pulses with 30 s of purge time inbetween pulses.

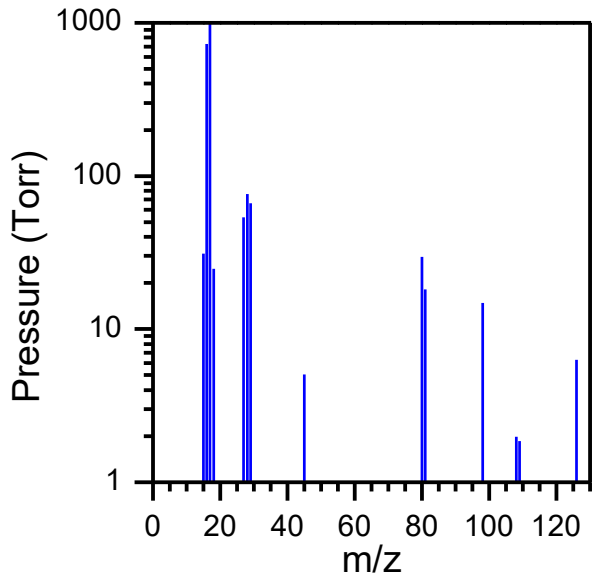

Figure S3. Mass spectra of DEPA measured directly from a cylinder heated to 115 °C.

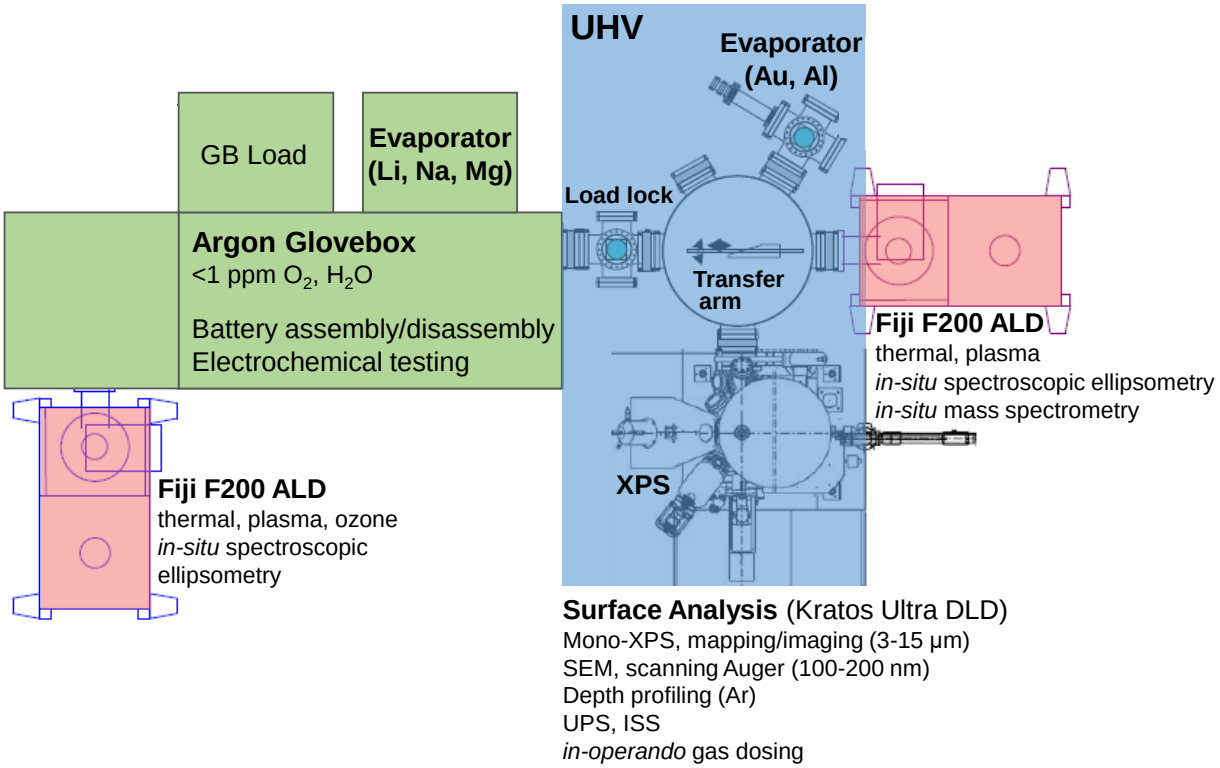

Figure S4. Overview of ANSLab. A schematic of the integrated vacuum system used for experiments described in the main text. ALD-grown samples can be transferred directly from the ALD chamber to the XPS all in a UHV environment. Samples can also be exposed to thermal evaporation and moved to an Ar glovebox for characterization without air exposure.

***In-Operando* Mass Spectrometry of ALD NaPON Process:**

Initial QMS data for the ALD NaPON process is displayed in Figure S5. A large peak at *m/z* 59 is observed for each NaO^{t}Bu pulse and DEPA pulse, agreeing with the detection of *tert*-butanol in the ALD LiPON process. Subtle peaks are observed at *m/z* 28 and 45 during the first DEPA pulse, but are difficult to detect in following DEPA pulses. These peaks agree with those in the DEPA pulse of the LiPON process, in which ethane (*m/z* 28) and ethanol (*m/z* 45) are released as products when reacting with LiO^{t}Bu on the surface. This supports a similar mechanism for ALD growth of NaO^{t}Bu-DEPA as LiO^{t}Bu-DEPA. It is noted that the intensities of each mass fragment are lower and the overall pressure measured is higher than that of the *in-operando* QMS data for the LiPON process in the main text. This is because the needle valve was removed between the ALD reactor and the QMS, which prevented the use of the high sensitivity low-vacuum valve in the QMS as described in Figure S1. Additionally, a modified recipe was not implemented to thoroughly characterize the time-resolved QMS data for the NaPON process as in the LiPON process, which made distinguishing of reactants and byproducts much more clear. This was a first pass to test if our theory that NaPON proceeds in a similar reaction mechanism to LiPON, which we have confirmed but will certainly provide more extensive characterization in a following publication.

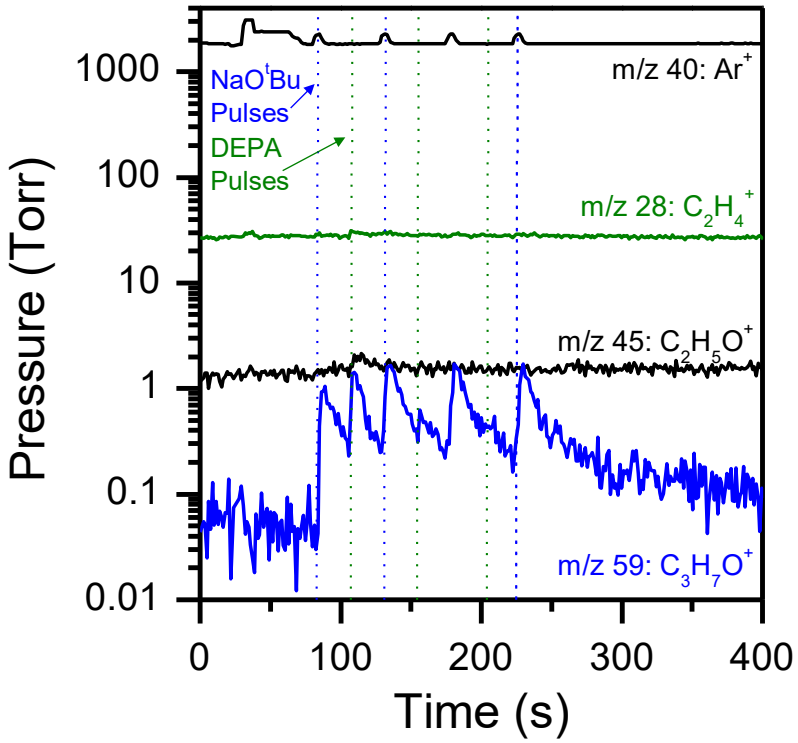

Figure S5. Mass spectra of the NaO^{t}Bu-DEPA NaPON process. NaO^{t}Bu was pulsed for 5 s and DEPA for 2 s, with 20s purges in between each pulse.

Supporting References:

1. A. J. Pearse, T. E. Schmitt, E. J. Fuller, F. El-Gabaly, C.-F. Lin, K. Gerasopoulos, A. C. Kozen, A. A. Talin, G. Rubloff and K. E. Gregorczyk, *Chemistry of Materials*, 2017, **29**, 3740-3753.
2. R. B. Nuwayhid, A. Jarry, G. W. Rubloff and K. E. Gregorczyk, *ACS Applied Materials & Interfaces*, 2020, **12**, 21641-21650.