Electronic Supplementary Material (ESI) for Chemical Communications.

Electronic Supplementary Information (ESI)

Electronic properties of lithium-ion conductive amorphous lithium phosphorus oxynitride

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1. Experimental setup of bias-controlled RF magnetron sputtering coupled with substrate cooling equipment

Fig. S1 shows the schematic of the bias-controlled RF magnetron sputtering system with a substrate cooling system.

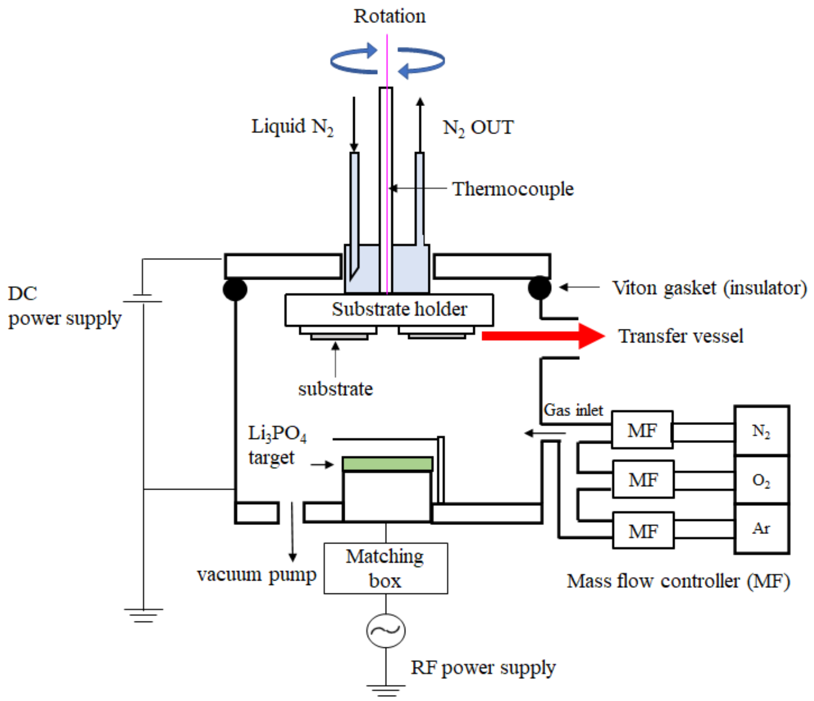

Fig S1. Schematic of the bias-controlled RF magnetron sputtering system with a substrate cooling system.

2. EIS analysis of Pt/LiPON/Li asymmetrical cell

Fig. S2a-2d summarizes the EIS spectra of the Pt/LiPON/Li asymmetrical cells, where the LiPON films are prepared for 15 h under N_2+O_2 (4:1 in vol) atmosphere at the bias of (a) 0V, (b) -2 V, (c) -4 V, and (d) -6 V. Each spectrum shows one semicircular arc at the high-frequency region, followed by a straight line to the real axis at lower frequency region. Each semicircular arc, however, will be combined with two semicircular arcs: solid electrolyte resistance and Li/solid electrolyte interfacial resistance. Distribution of relaxation times analysis (DRT) detects two relaxation time for the semicircular arcs, which is denoted as DE1 (solid electrolyte resistance) and DE2 (Li/solid electrolyte resistance). Table S1 summarizes the DRT analyzed data for the Pt/LiPON/Li cell. Also, an equivalent circuit model is shown in it, where R is the electric circuit resistance of almost "0". The DRT analysis was carried out for the frequency range of each semicircular arc (100 kHz-10 kHz for the LiPON prepared at the bias of 0 V and 100 kHz-1 kHz for the other LiPONs). The LiPON film prepared at the bias of 0 V appeared only one distribution peak (Fig. S2e), probably because the semicircular arc did not converge near the real axis on the lower frequency side. Other LiPONs showed two kinds of distribution peaks (Fig. S2 f-h). DRT analyzed data are summarized in Table S1, where DE-1R is assigned to LiPON resistance, and DE-2-R is assigned to Li/LiPON interface resistance [1]. Also, values of DE-T (relaxation times) and DE-P (depression factors) are also displayed in Table S1. Major resistance of the semicircular arc is DE-1, and the ionic conductivity of each LiPON film is calculated using the DE1-R values of the LiPON films, which are summarized in Table 1 in the article.

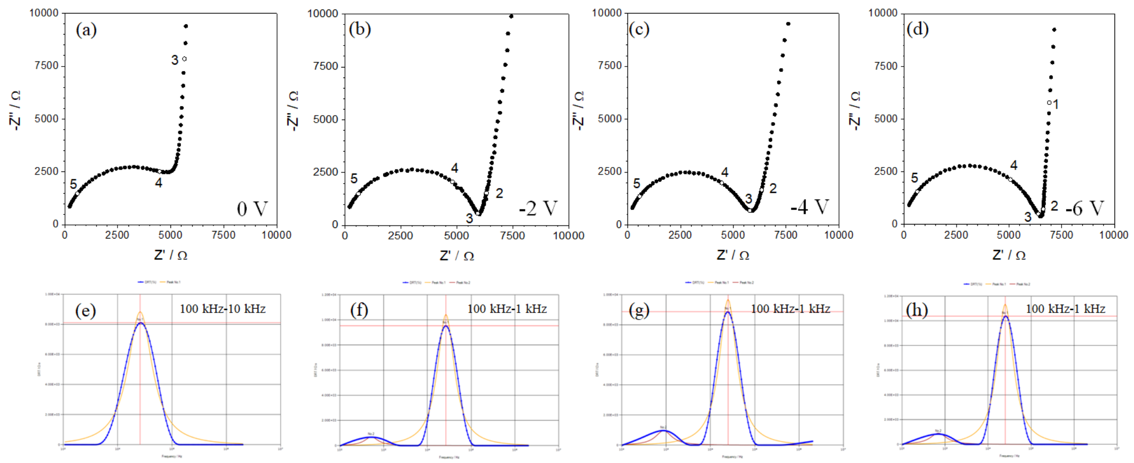

Fig S2. EIS spectra of Pt/LiPON/Li cells prepared at the bias of (a) 0V, (b) -2 V, (c) -4 V, and (d) -6 V. Numbers mean the data point measured at 10^n Hz. DRT analyzed data of each semicircular arc is shown in (e) 0 V, (f) -2 V, (g) -4 V, and (h) -6 V.

Table S1. Summaries of DRT analyzed data of LiPON films prepared at different DC biases. The inset shows the equivalent circuit model of the Pt/LiPON/Li cell, where R0 is the electric circuit resistance (almost "0"), DE1 is LiPON, and DE2 is Li/LiPON interface. DE2 was not detected (ND) from the LiPON prepared at the bias of 0 V (Fig. S2e). DE-1R: LiPON resistance, DE-2-R: Li/LiPON interface resistance, DE-T (relaxation time), DE-P (depression factor).

electric circuit resistance LiPON Li/LiPON

voltage	DE1-R (Ω)	DE1-T (F)	DE1-P	DE2-R (Ω)	DE2-T (F)	DE2-P
0 V	5929	6.12E-6	0.90	ND	ND	ND
-2 V	5841	5.90E-6	0.93	850	3.0E-4	0.89
-4 V	5635	6.39E-6	0.91	1220	4.1E-4	0.87
-6 V	6211	6.10E-6	0.92	467	1.6E-4	0.84

[1] Y. Iriyama, T. Kako, C. Yada, T. Abe, and Z. Ogumi, *Solid State Ionics*, 2005, **176**, 2371-2376.

3. XPS spectra of LPN-xs

Figure S3 summarizes the XPS spectra of Li 1s, P 2p, O 1s, C 1s, N1s, and Pt 4f of the LPN-xs. All the data were measured without surface etching under the neutralizer radiation.

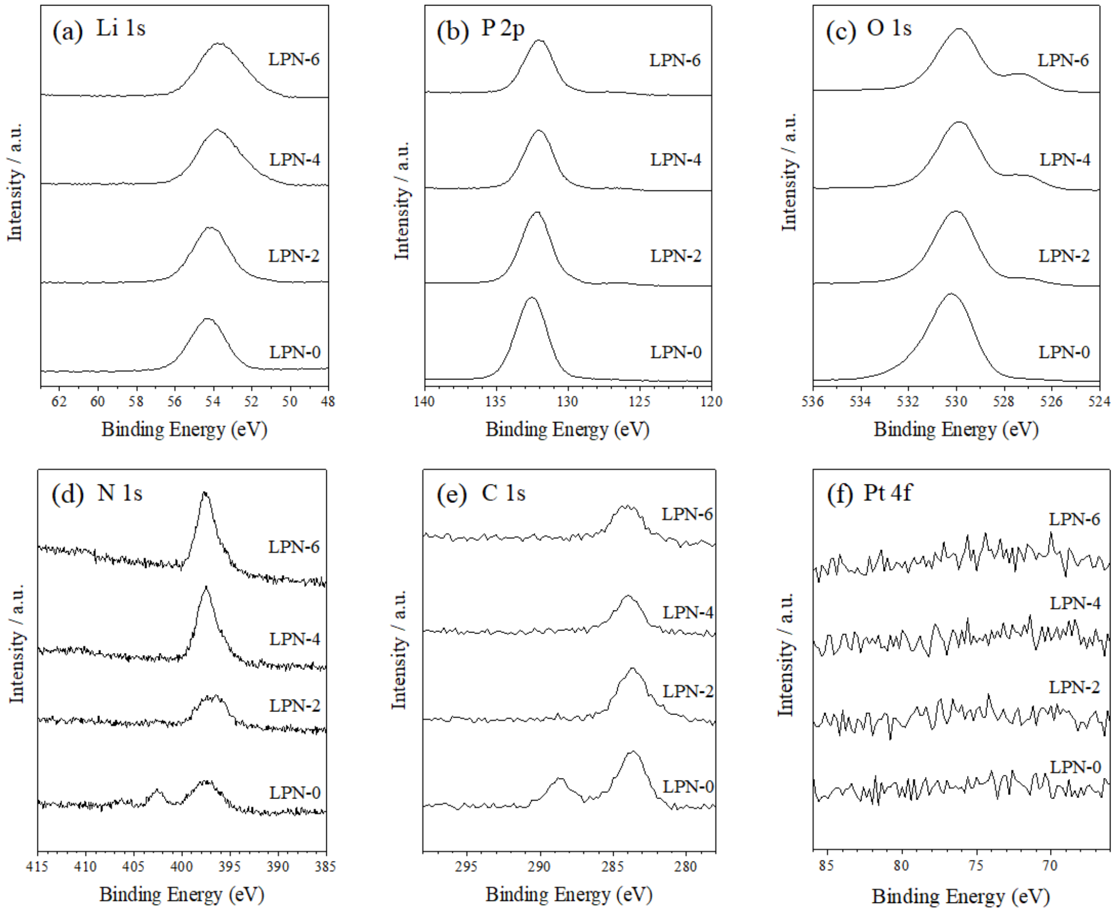

Fig. S3 XPS spectra of (a) Li 1s, (b) P 2p, (c) O 1s, (d) C 1s, (e) N1s, and (f) Pt 4f of the LPN-*x*s.

4. Cross-sectional FE-SEM images of LPN-*x*s

Fig. S4 summarizes the cross-sectional FE-SEM images of LPN-*x*s, where Pt layer was deposited by RF magnetron sputtering on each LPN-x to reduce charge-up during the FE-SEM observations. The substrates were Si wafers with Ti (ca. 3 nm)/Pt (ca. 60 nm) coating layers as conductive films. Number in each FE-SEM image is the averaged thickness of LPN-*x*s measured at several points.

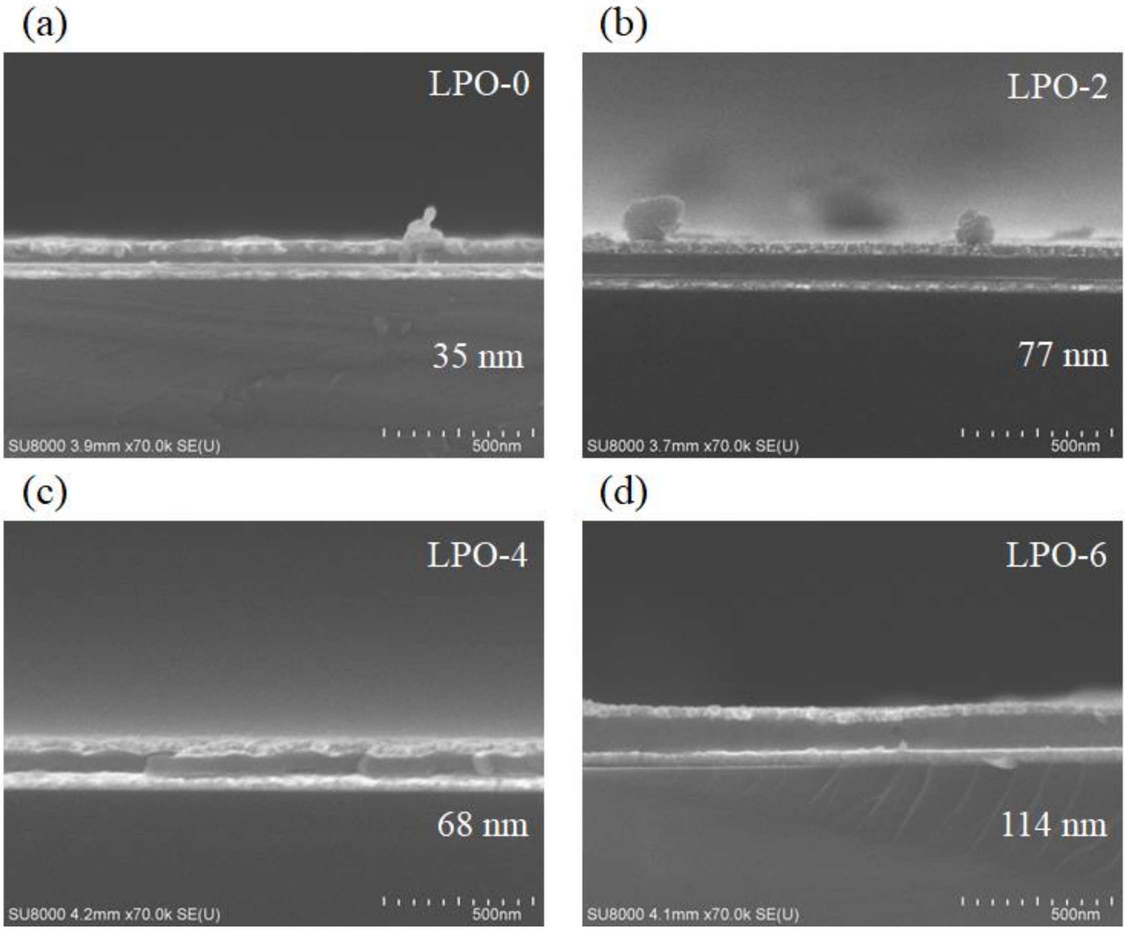

Fig. S4 Cross-sectional FE-SEM images of the LPN-xs. (a) LPN-0, (b)LPN-2, (c)LPN-4, and LPN-6.

5. O1s spectra of LPN-*xs* and LPN-2Ar

Fig. S5 summarizes the O1s spectra of LPN-*xs* and LPN-2Ar.

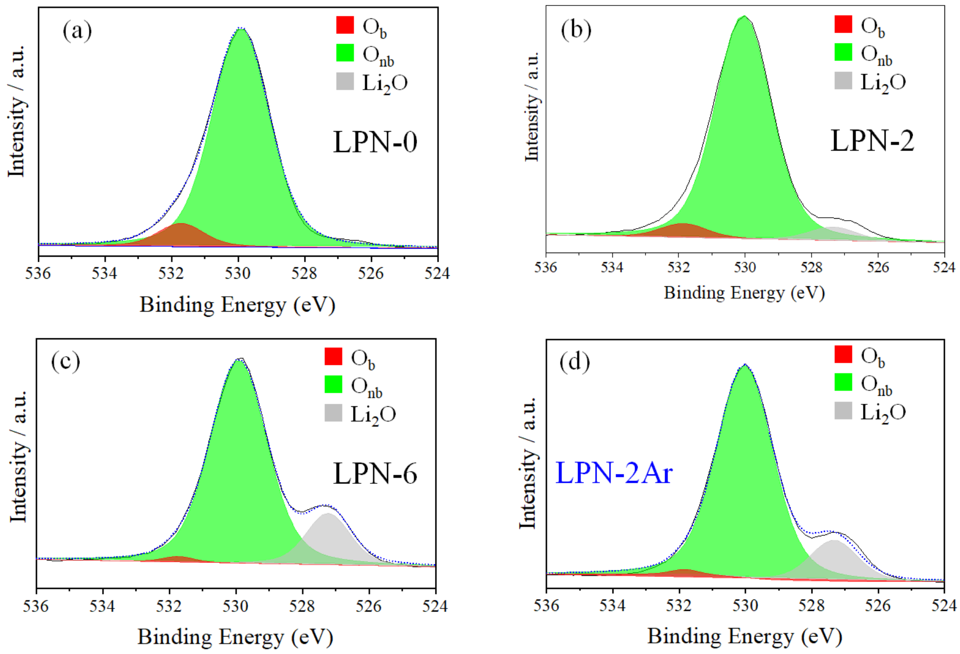

Fig. S5 O1s spectra of (a) LPN-0, (b) LPN-2, (c) LPN-6, and (d) LPN-2Ar. All the O1s spectra are deconvoluted to O_{nb} (green), O_b (red), and Li_2O (grey) by CASA XPS. Dotted blue lines are the fitting data from the deconvoluted peak.

6. UPS/LEIPS combined spectra of LPN-2Ar and the values of CBM, VBM, and EF.

Fig. S6(a) shows the UPS-LEIPS combined spectra of LPN-2Ar. Values of CBM, VBM, E_F, Δ_{BG}, and Δ is summarized in Fig. S6(b).

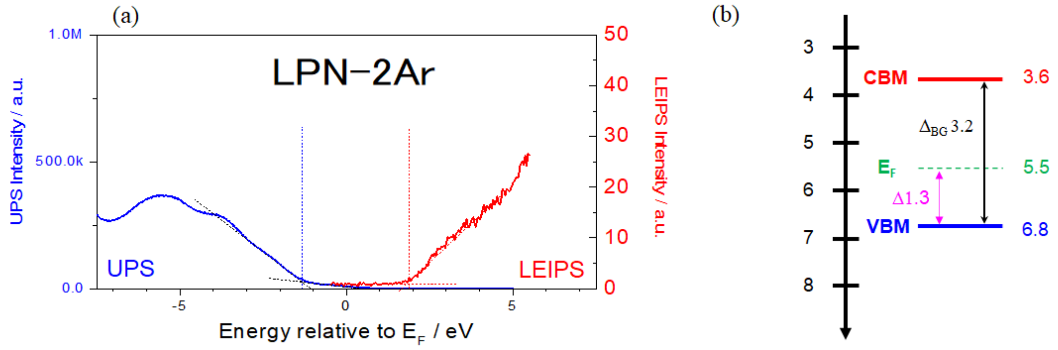

Fig. S6 (a) UPS (blue) and LEIPS (red) combined spectra of LPN-2Ar. (b) Summary of VBM (blue), CBM (red), and E_F (green) absolute electron energy values against vacuum. The CBM-VBM gap (Δ_{BG}: black), and E_F-VBM gap (Δ: purple) are also shown in it.