## A Thin and High Strength Composite Polymer Solid-State Electrolyte

## with Highly Efficient and Uniform Ion Transport Network

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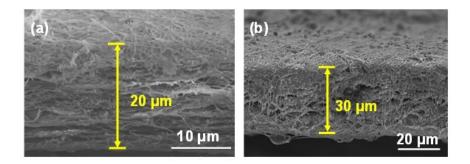


Fig. S1. Cross-section SEM images of (a, b) the PAN network

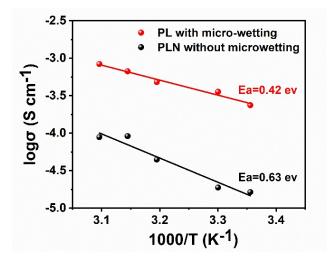
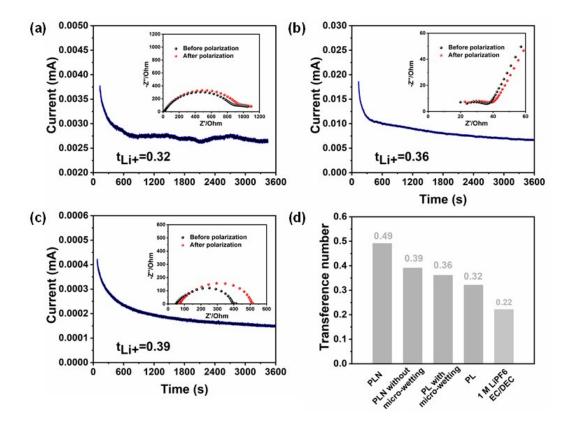


Fig. S2.  $E_a$  of PLN without micro-wetting and PL with micro-wetting.



**Fig. S3**. Transference number of (a) PL, (b) PL with micro-wetting, (c) PLN without micro-wetting and (d)1 M LiPF<sub>6</sub> EC and DEC liquid electrolyte

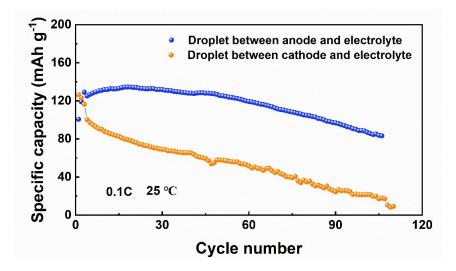


Fig. S4. Galvanostatic cycles of the PEO-based batteries operating at 0.1 C, 25 °C.

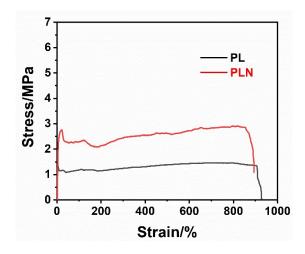
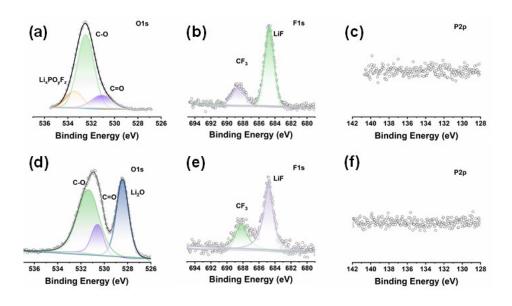
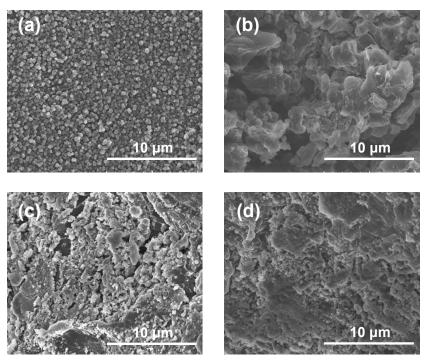


Fig. S5. Stress-strain curves of PL and PLN solid electrolytes.

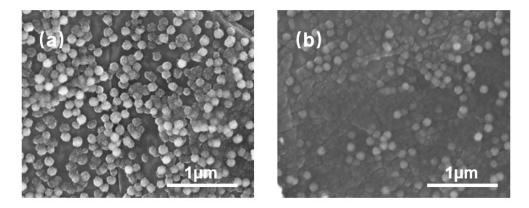
The PLN electrolyte with rigid PAN network shows enhanced mechanical properties (2.73 MPa) than that of PL (1.28 MPa).



**Fig. S6**. XPS spectra of (a) O 1s (b) F 1s and (c) P 2p on the surface of Li anode from Li/PL with micro-wetting/Li after 40 cycles; XPS spectra of (d) O 1s (e) F 1s and (f) P 2p on the surface of Li anode from Li/PLN without micro-wetting/Li after 40 cycles.



**Fig. S7**. Typical top-view SEM images of Li anode with (a) PLN, (b) PL, (c) PL with micro-wetting and (d) PLN without micro-wetting SSEs.



**Fig. S8**. High magnification SEM images of the Li anode with PLN electrolyte in the end of (a) charge and (b) discharge processes.

	Resistance ( $\Omega$ )	Thickness (µm)	Ionic conductivity
			(×10 <sup>-4</sup> S/cm)
PL	1600	100	0.031
PLN with out	832	60	0.036
micro-wetting			
PL with micro-	56	100	0.892
wetting			
PLN	22	55	1.25

## Table S1. Ionic conductivity of SSEs