Supporting Information

A Layer-by-Layer (LbL) Assembly Strategy for Reinforcing the Mechanical Strength of an Ionogel Electrolyte without Affecting Ionic Conductivity.

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Experimental Section

Materials

PVDF-co-HFP (Aldrich, M_n ~130,000), methyl isobutyl ketone (MIBK, Acros, 99.5% analysis grade), LiTFSI, triblock copolymer Pluronic® F-127 (M_n ~12,000), 1,3,5-trimethylbenzene, K_2SO_4, tetramethoxysilane, (3-mercaptopropyl)trimethoxysilane, 1-methylpyrrolidine, 1-bromobutane were purchased from Sigma-Aldrich and used as received. Nafion (ion powers inc), Poly (diallyldimethylammonium chloride) (Mw=400,000- 500,000, sigma aldrich) and poly (styrene sulfonic acid) (Mw= 130, 000, sigma Aldrich) were used as received.

Synthesis of ionic liquids and lithiated polyanions

Ionic liquid 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonimide) (BMPy-TFSI) was synthesized following the published procedure.[1] Nafion and poly (styrene sulfonic acid) were neutralized by titrating a 0.5 M LiOH solution to obtain the lithiated form of these polyanions.

Fabrication of pseudo-solid membrane via layer-by-layer (LbL) assemblies

PVDF-co-HFP (30% by weight), 0.5 molal (m) LiTFSI in BMPy-TFSI (70% by weight) were dissolved in acetone at 50° C for 5 hours to make the homogeneous solution. The polymer-ionic liquid electrolytes solution was cast on the glass petri-dish, and the solvent was evaporated slowly under the ambient condition. Thus, fabricated membranes were dried at 100°C for 12 hours for removing the trapped moisture and the solvent and hereafter referred to as an ionogel. After drying the membrane, ultrathin coating of polyanions and polycations were carried out via layer by layer assemblies. (Scheme 1). At first, ionogel was dipped into the 1% solution of lithiated Nafion/ lithiated poly (styrene sulfonic acid) for 30 seconds. Then, the membrane was

washed with DI water to remove loosely attached polymer chains. After air-drying the layer, it was dipped into a 1 % solution of poly (diallyldimethylammonium chloride) for 30 seconds, followed by washing in deionized water to remove loosely held polymer on the surface. This process was repeated five times. The outer layer of the membrane was polyanionic polymers, either lithiated Nafion or lithiated poly (styrene sulfonic acid). Then, the membrane was dried in a vacuum oven at 120°C for ten days to remove the trapped water and stored in an argon-filled glove box (moisture < 0.5 ppm). Thus, fabricated membranes were referred to as LbL-LiNaf (if the outer layer is lithiated Nafion) and LbL-LiPSS (if the outer layer is lithiated poly (styrene sulfonic acid).

Membrane Characterization

Infrared (IR) spectroscopy was conducted on a Nicolet IS50 FT-IR (ATR) spectrometer in the range of 4000-500 cm^{-1}. The surface morphology of uncoated ionogel and ionogel with LbL coating was investigated by scanning electron microscopy (SEM). Stress–strain properties were measured on a dynamic mechanical analyzer (DMA Q800) using a rectangular shape (~4.0 mm × ~3.0 mm) membrane. The stress-strain analysis was conducted under controlled force mode at constant temperature (25 °C) with a force ramp rate of 0.1 N min^{-1}.

Electrochemical Measurements

The conductivity of the samples was measured using the Alpha-A analyzer from Novocontrol in a frequency range of 10^{-1} Hz to 10^{6} Hz. The plate capacitor was used with two parallel round metallic electrodes, and the distance between them equal to the membrane thickness. The samples were placed in the area between the electrodes and measured with an ac voltage amplitude signal of 0.1 Vrms. A Quattro temperature controller by Novocontrol was used for different temperature measurements. The temperature stabilization at each temperature was 1000

sec to maintain a stable temperature within 0.2 K. The temperature dependencies of ionic conductivity were fitted by Vogel-Fulcher-Tamman (VFT) behavior $\sigma = \sigma_0 \exp\left(-B/(T - T_0)\right)$, and their fitting parameters are given in table S1.

Table S1 VFT fit parameter and standard error obtained by fitting the temperature-dependent ionic conductivity of uncoated ionogel and LbL reinforced ionogel using the VFT equation.

Name	σ_0[S/cm]		B[kJ/mol]		T_0[K]	
	Value	Std. Error	Value	Std. Error	Value	Std. Error
LbL-LiNaf	0.11	0.03	5.54	0.07	183.83	0.006
Ionogel	0.59	0.04	8.40	0.01	160.79	0.001
LbL-LiPSS	0.27	0.02	7.11	0.05	169.83	0.004

Linear sweep voltammetry (LSV) was conducted using Li||LbL-membrane||Pt cells from 2.0 V to 6.0 V *vs*. Li/Li^+ with a scan rate of 10 mV/s. Symmetric Li||LbL-LiNaf||Li cells were assembled in an argon-filled glove box (moisture and oxygen < 0.5 ppm) and used to study interfacial stability and measure lithium transference number ($\mathbf{t_{Li}^+}$), in which membranes were sandwich between two lithium discs as a non-blocking electrode. Combination of dc polarization and ac impedance measurements was used to calculate t_{Li}^+ using the following equation:[2-3]

$$t_{Li}^+ = [I_s (\Delta V - I_i R_i)]/[I_i (\Delta V - I_s R_s)]$$

where ΔV is the polarization bias voltage, I_i, R_i, and I_s, R_s are initial and steady-state currents and resistance, respectively.

Symmetric Li||LbL-LiNaf||Li cells were periodically cycled (3 hours charge, 1 hr rest followed by 3 hrs discharge and 1 hr rest) to determine interfacial stability. $LiFePO_4$ (LFP) cathodes were prepared by homogeneously mixing LFP, carbon black (CB 45), and PVDF in NMP in weight ratio 7:2:1, cast on aluminum foil and dried at 100 °C for 12 hrs in a vacuum oven. The loading of active material was around 3.0-3.5 mg cm^{-2} with an electrode area of 1.27 cm^2. Coin cells were assembled using lithium as anode and LFP as the cathode and LbL

membranes as the electrolyte inside the high purity argon gas (oxygen and moisture < 0.5 ppm) filled glove box. The cycling performance was carried out on Land Battery tester over a voltage range from 2.5 V–4.0 V at a scan rate of 0.1 C at 60 °C and cyclic voltammetry was conducted in on a bio-logic VSP instrument from 2.5 V–4.0 V at a scan rate of 0.04 mV s^{-1}.

FT-IR Analysis of LbL membranes

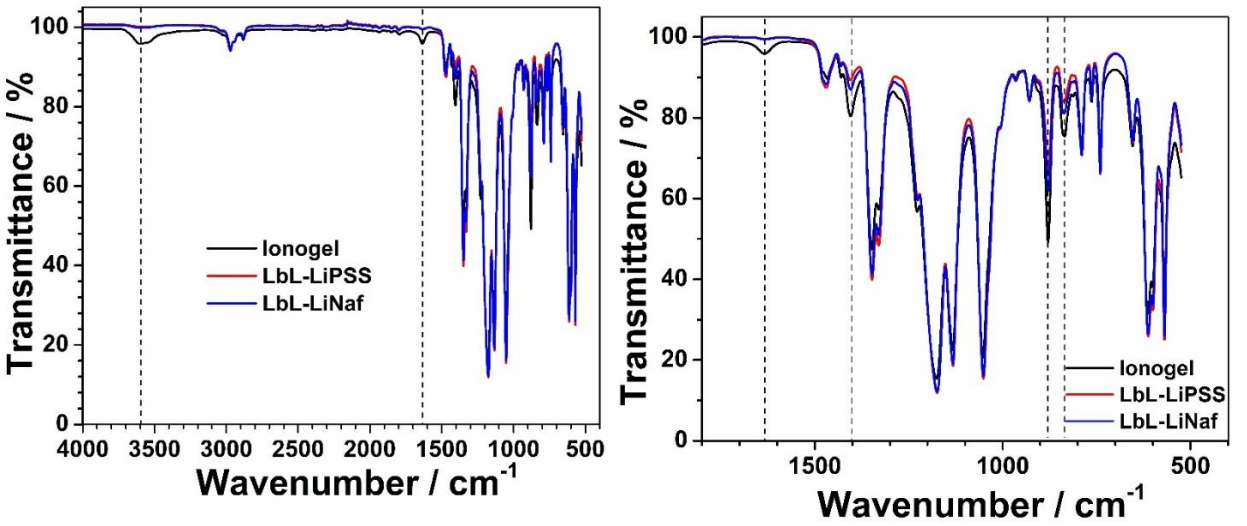

Figure S1. FT-IR spectra of ionogel, LbL-LiPSS, and LbL-LiNaf showing the electrostatic interaction

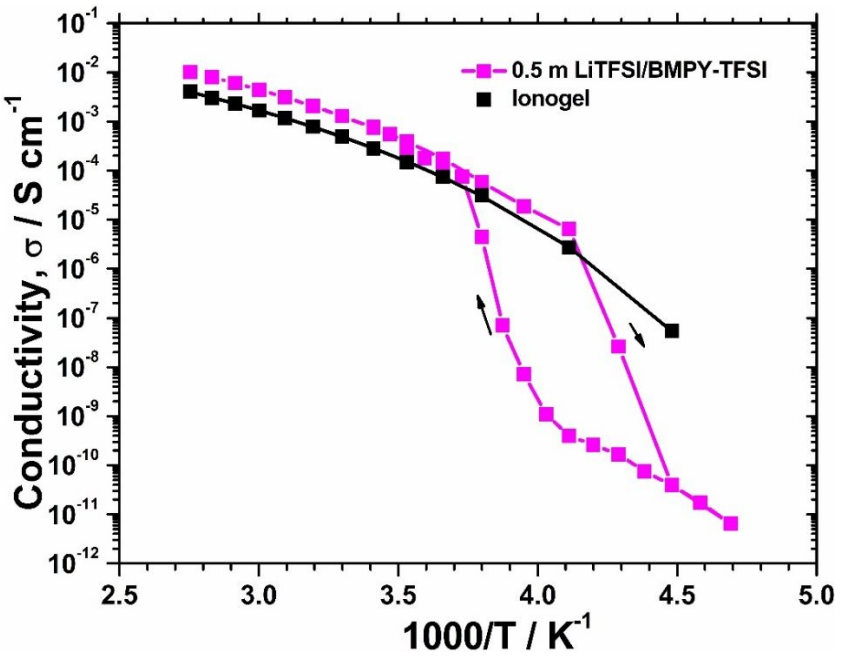

Figure S2. Temperature dependencies of ionic conductivity of an ionogel, and 0.5 m LiTFSI / BMPy-TFSI

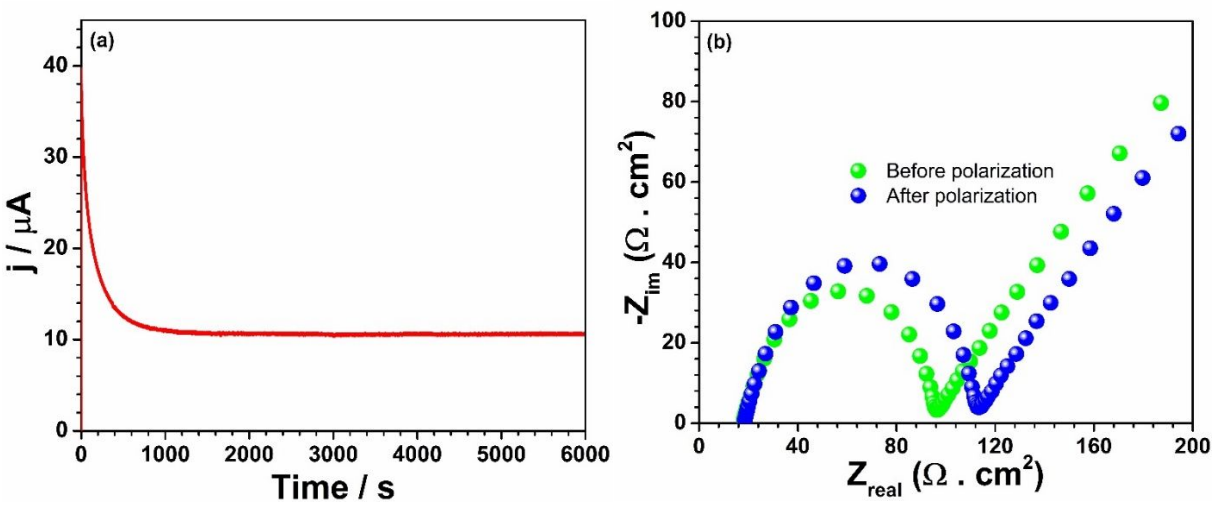

Figure S3. (a) DC polarization of LbL-LiNaf; and (b) AC impedance spectra of LbL-LiNaf before and after 10 mV DC polarization measured at 60 °C.

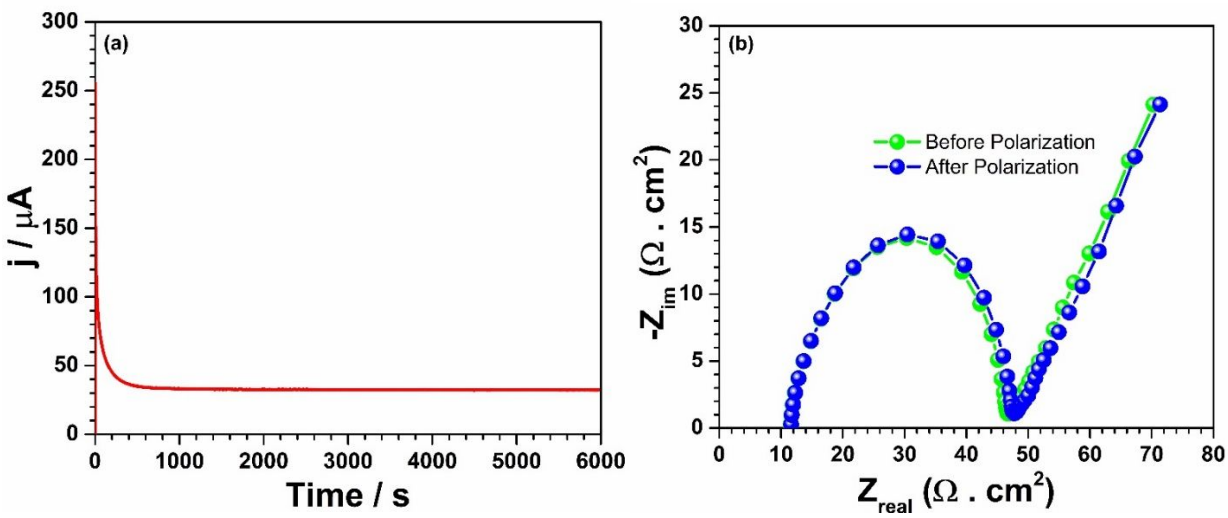

Figure S4. (a) DC polarization of ionogel; and (b) AC impedance spectra of ionogel before and after 10 mV DC polarization measured at 60 °C.

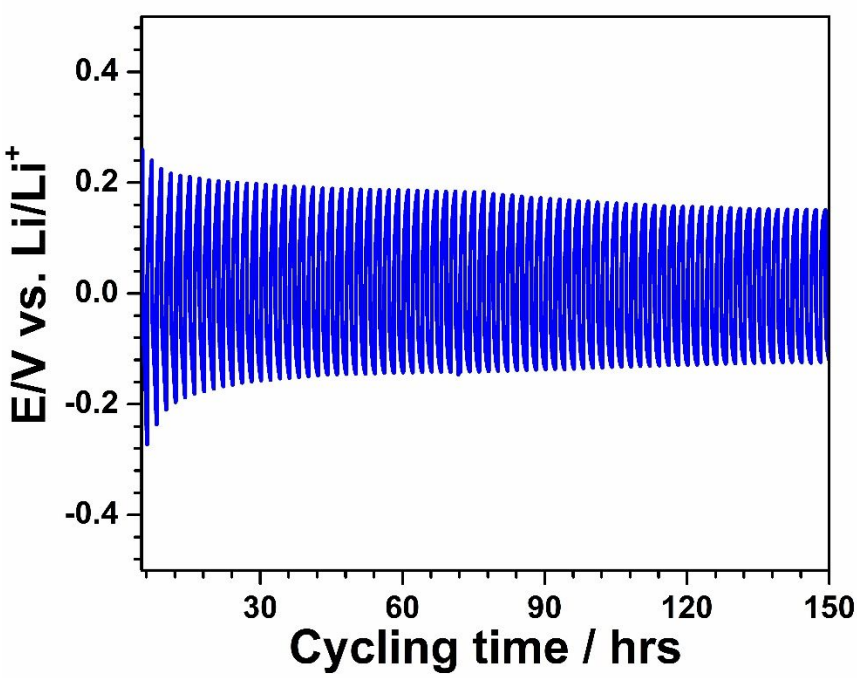

Figure S5. Cyclic performance of Li||LbL-LiNaf||Li cells at a current density of 0.1 mA cm^{-2} at 30 °C.

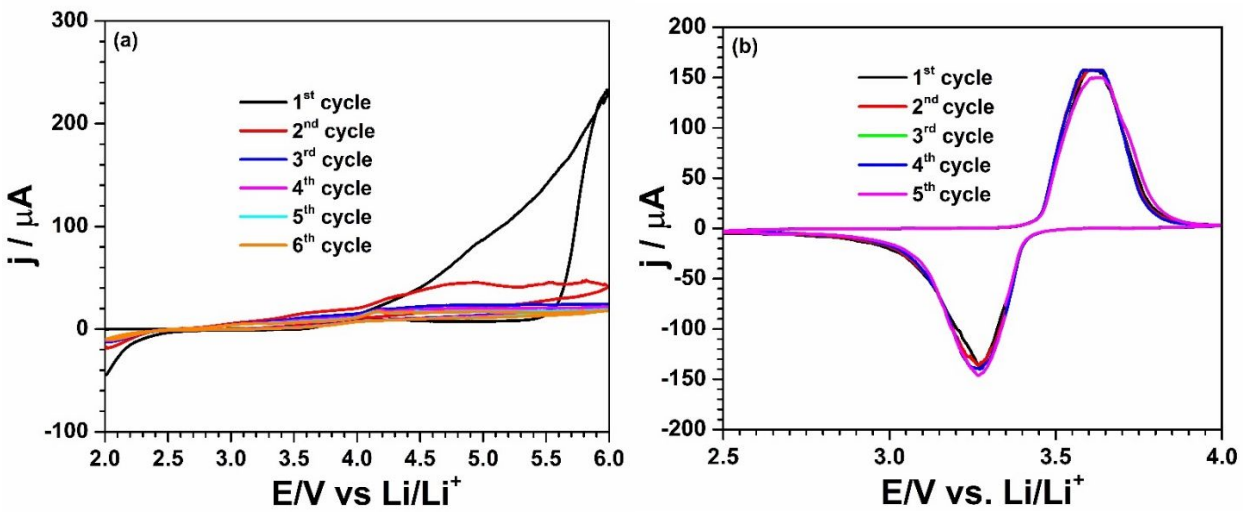

Figure S6. (a) CV plot of Li||LbL-LiNaf||Al at 0.1 mV s^{-1} scan rate; (b) CV plot of Li||LbL-LiNaf||LFP at 0.04 mV s^{-1} scan rate.

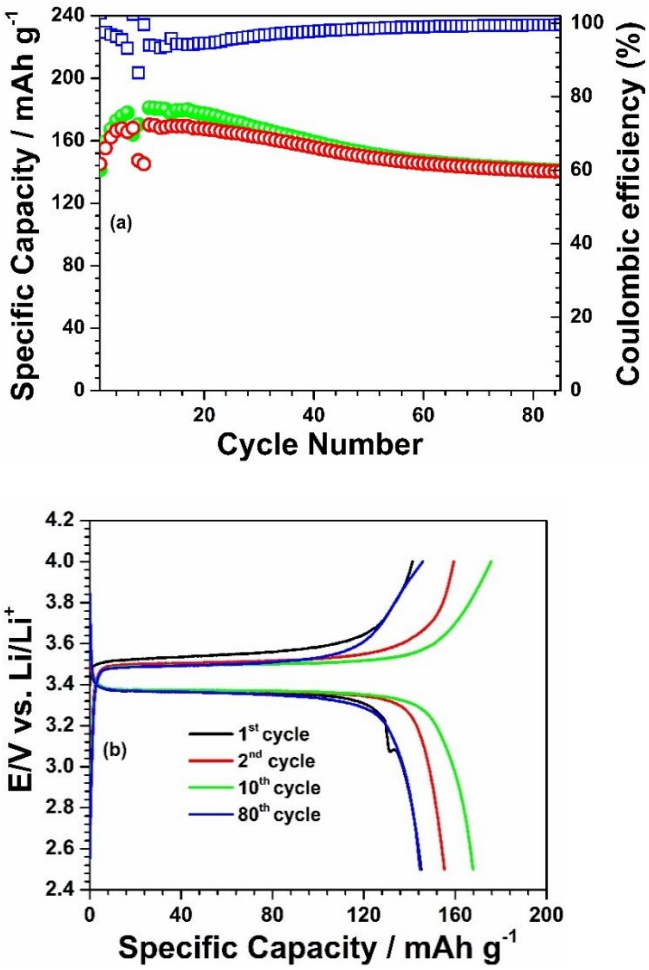

Figure S7. Electrochemical performance of Li||LbL-LiNaf||LFP at 60 °C. Showing (a) charge and discharge capacity and (b) charge and discharge profiles at a current rate of 0.1 C.

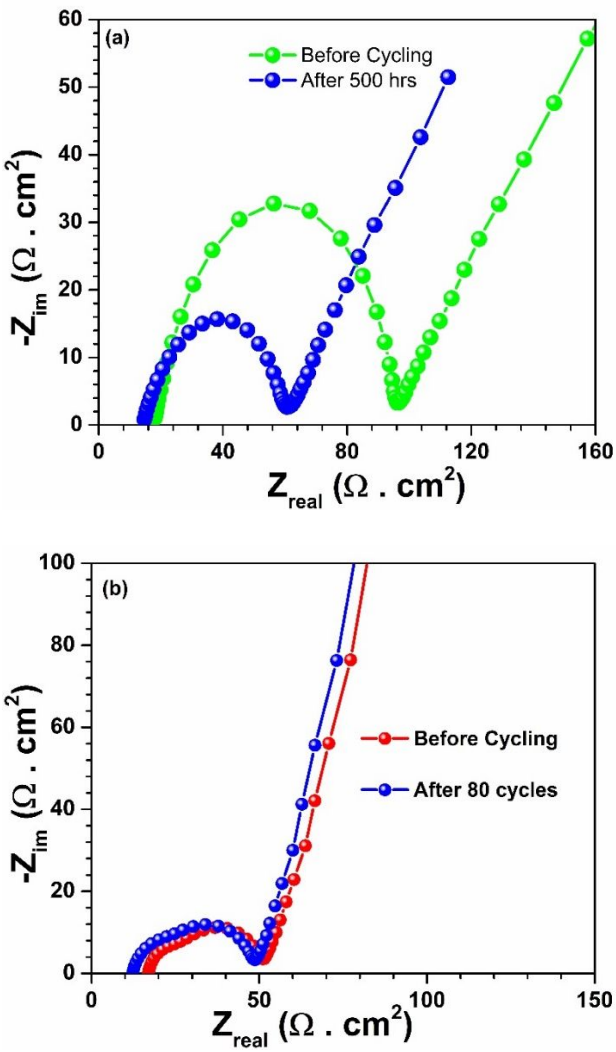

Figure S8. (a) Electrochemical impedance spectra of Li||LbL-LiNaf||Li showing the drop of bulk as well as interfacial resistance; (b) Electrochemical impedance spectra of Li||LbL-LiNaf||LFP showing the stable electrode/electrolyte interface and excellent electrode compatibility of the membrane.

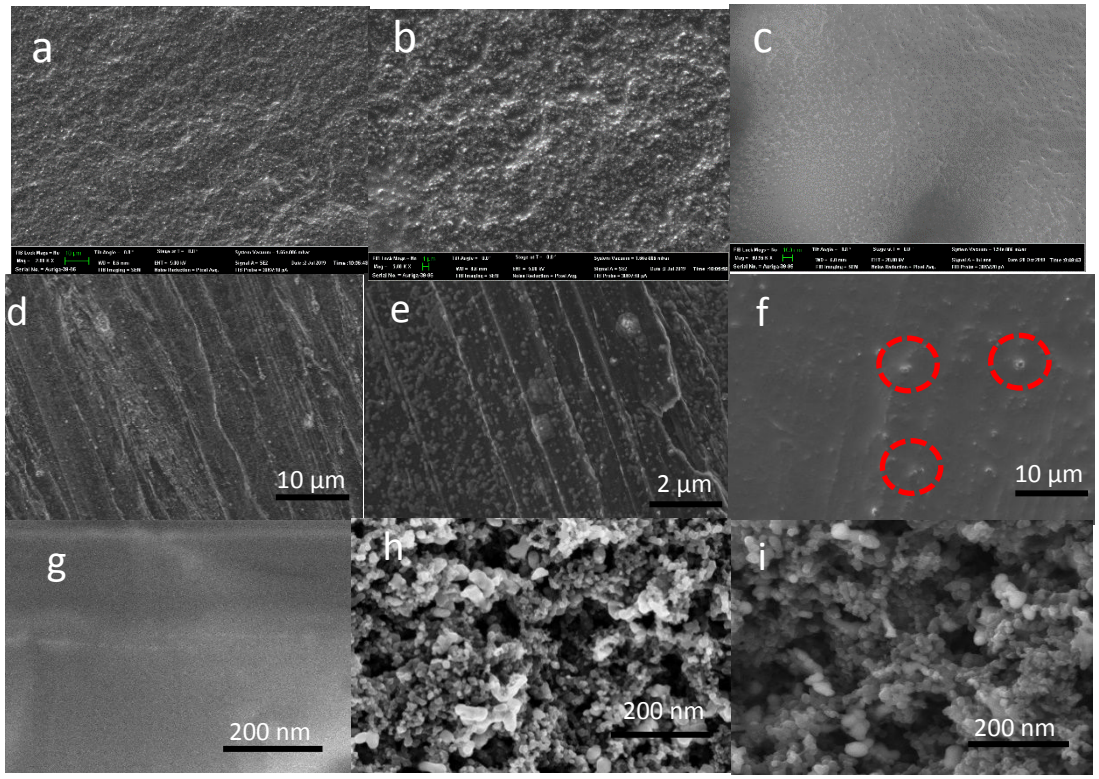

Figure S9. Comparison of LbL-LiNaf, Lithium anode, and $LiFePO_4$ (LFP) cathode before and after cycling at 60 °C. (a) fresh LbL-LiNaf; cycled LbL-LiNaf during Li plating/striping experiment after 500 hrs (b and c); Fresh (d, and e) and cycled Li metal anode (f, and g); fresh (h) and cycled LFP (i).

References

1. Prasad Thapaliya, B.; Do-Thanh, C.-L.; Jafta, C. J.; Tao, R.; Lyu, H.; Borisevich, A. Y.; Yang, S.; Sun, X.-G.; Dai, S., Simultaneously Boosting the Ionic Conductivity and Mechanical Strength of Polymer Gel Electrolyte Membranes by Confining Ionic Liquids into Hollow Silica Nanocavities. *Batteries & Supercaps* **2019,** *0* (ja).
2. Evans, J.; Vincent, C. A.; Bruce, P. G., Electrochemical measurement of transference numbers in polymer electrolytes. *Polymer* **1987,** *28* (13), 2324-2328.
3. Zugmann, S.; Fleischmann, M.; Amereller, M.; Gschwind, R. M.; Wiemhöfer, H. D.; Gores, H. J., Measurement of transference numbers for lithium-ion electrolytes via four different methods, a comparative study. *Electrochim. Acta* **2011,** *56* (11), 3926-3933.