Supporting Information

In situ formed LiF protective layer on Li metal anode with solvent-less cross-linking.

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Experimental section

2-(perfluorooctyl)ethyl acrylate (Fluoryx Labs) was used as the PL. Tert-Butyl peroxypivalate (Sigma Aldrich) was used as the initiator. 2-(perfluorooctyl)ethyl acrylate and tert-Butyl peroxypivalate were mixed in a mass ratio of 10:1 to form the curing mixture. PE separator, PVdF, and Super P were bought from Asahi Kasei Chemicals Corporation, Arkema, and MTI Korea, respectively. LiFePO$_4$ was obtained from Hanwa Chemicals. 1 M of LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol) was obtained from PANAX ETEC Co. Ltd and stored in an argon-filled glove box. Coin cells with the 2032-type configuration were assembled. The LiFePO$_4$ slurry was prepared by mixing LiFePO$_4$, Polyvinylidene fluoride (PVDF) and super P in the ratio of 8:1:1 with N-Methyl-2-pyrrolidone (NMP). 2.2 g of NMP was added based on 1 g of LiFePO$_4$ slurry to make proper viscosity. The slurry was coated on aluminum foil and then dried in a convection oven at 120 °C for 4 hours. This electrode pressed under 80% of original thickness with pressing machine. This pressed electrode was dried overnight in a vacuum oven at 120 °C. Loading density of this electrode is 1.2 mg cm$^{-2}$. 
Scheme S1. Polymerization mechanism of 2,2-(perfluorooctyl)ethyl acrylate
**Fig. S1** Atomic percentages of F-rich film fabricated on Li metal surface.
Fig. S2 Energy-dispersive X-ray spectroscopy (EDS) mapping images of in situ LiF PL on Li metal
**Fig. S3** X-ray diffraction (XRD) analysis of in situ LiF PL on Li metal
Fig. S4 Picture of measuring thickness of in situ LiF PL. (a) Thickness of single layer of Cu/Li (b) Thickness of 10 layers of Cu/Li (c) Thickness of 10 layers of Cu/Li coated with in situ LiF PL (d) Images of measuring thickness of stacked Cu/Li.
Fig. S5 SEM-EDS analysis results of bare Li metal (left) and Li metal with in situ LiF PL (right).
Fig. S6 Surface images of bare Li metal after 100 cycles (left) and Li metal with in-situ LiF PL after 100 cycles (right).
Fig. S7 (a) Equivalent circuit of Li/Li symmetrical cell. AC impedance spectra of bare Li metal and Li metal with in situ LiF PL.
Fig. S8 X-ray photoelectron spectroscopy (XPS) results of bare Li metal after 100 cycles (left) and Li metal with in situ LiF PL after 100 cycles (right).
**Fig. S9** Charge/discharge profiles of (left) bare Li metal and (right) Li metal with in situ LiF PL with LiFePO$_4$. 
Fig. S10 Images of pouch cell.