Supplementary Information

Facile ex-situ formation of a LiF-polymer composite layer as an artificial SEI layer on Li metal by simple roll-press processing for carbonate electrolytes-based Li metal batteries

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Supplementary Note 1: Calculation of porosity of Li anode after deposition

The porosity of deposited Li metal in Figure 3 was calculated by dividing the measured height by the theoretical height. In the case of depositing 1mAh cm-2 of lithium, the theoretical height of lithium metal is 4.85 micrometer according to equation (1). After depositing the lithium metal, the height was measured by observing the SEM image. The porosity was measured according to equation (2) by dividing the measured height by the theoretical height.

(1) Calculation of specific thickness of Li metal (h_{Li}^0)

$$h_{Li}^0 = \frac{10^5 \ [\frac{\mu m}{cm}]}{\rho_{Li} \ [\frac{g}{cm^3}] \ast Capa_{Li} \ [\frac{mAh}{g}]}$$

$$= \frac{10^5 \ [\frac{\mu m}{cm}]}{0.534 \ [\frac{g}{cm^3}] \ast 3860 \ [\frac{mAh}{g}]}$$

$$= 4.854 \ \mu m \ [\frac{cm^2}{mAh}]$$

Where, ρ_{Li} and $Capa_{Li}$ are theoretical density and gravimetric capacity of Li metal, respectively.

(2) Calculation of porosity by deposited height of Li metal from SEM image

Porosity $= 100 \ast (\ 1 - (h_{Li}^0 \ast 1 \ \text{mAh cm}^{-2})/h_{Li}^{evaluated} \ )$

$= 100 \ [\%] \ast (\ 1 - 4.854 \ \mu m / \ 6.8 \ \mu m)$

$= 28 \ \%$

Supplementary Note 2: Calculation of average Coulombic efficiency of Li anode for full-cell

The average Coulombic efficiency (C.E) is calculated based on the total cycle number (n) and loaded Li capacity. The theoretical gravimetric specific capacity (C_{grv}) of Li metal is 3860 mAh g^{-1}. The density (ρ) of Li metal is 0.534 g cm^{-3}. So, the volumetric specific capacity of Li metal is calculated by below equation.

$$C_{vol} = C_{grv} \cdot \rho \quad (1)$$

$$= 3860 \ (\text{mAh g}^{-1}) \cdot 0.534 \ (\text{g cm}^{-3})$$

$$= 2061.24 \ \text{mAh cm}^{-3}$$

The average capacity loss can be calculated by dividing total capacity of Li metal by the number of stable cycle (n, where the C.E of cathode > 99%). The total areal capacity of Li metal is determined by equation (2).

$$C_{Li} = C_{vol} \cdot \text{thickness of the Li} \quad (2)$$

$$= 2061.24 \ (\text{mAh cm}^{-3}) * 0.05 \ (\text{cm})$$

$$= 103.1 \ \text{mAh cm}^{-2}$$

And the average capacity loss (C_{loss}) is calculated by equation (3, 3-1 and 3-2)

$$C_{loss} = C_{Li} / n \ (3)$$

$$C_{loss, LCO} = 103.1 \ \text{mAh cm}^{-2} / 177 = 0.5823 \ \text{mAh cm}^{-2} \ (3\text{-}1)$$

$$C_{loss, NCM} = 103.1 \ \text{mAh cm}^{-2} / 198 = 0.5207 \ \text{mAh cm}^{-2} \ (3\text{-}2)$$

The average capacity loss during one cycle implies irreversible capacity in the Li plating/stripping process for an average of one cycle. The average plating and stripping capacity of Li is the average cell capacity during stable cycle. For the Li || LCO and Li || NCM-811 cell in Figure 5, the average cell capacities are $C_{LCO, avg} = 3.2$ mAh cm^{-2} and $C_{NCM,}$

$_{avg}$ = 2.1 mAh cm^{-2}, respectively. Subsequently, the average C.E of Li metal for Li || LCO and Li || NCM-811 full cells are calculated by the equation (4, 4-1 and 4-2)

C.E (Li paired with cathode) = {areal capacity of cathode electrode – (CLi / n) } / areal capacity of cathode electrode (4)

C.E (Li paired with LCO) = { 3.2 mAh cm^{-2} - (103.1 mAh cm^{-2} / 177) } / 3.2 mAh cm^{-2}
= 81.8 % (4-1)

C.E (Li paired with NCM-811) = { 2.1 mAh cm^{-2} – (103.1 mAh cm^{-2} / 198) } / 2.1 mAh cm^{-2}
= 75.2 % (4-2)

Experimental section

LiF - Li and LiF@C - Li preparation Li metal (500 μm and 50 μm Wellcos, Korea) and PTFE film (200 μm, PTFE0200, Alphaflon, Korea) were pressed using a roll-press machine (WCRP-1015G, Wellcos, Korea) in an argon-filled glove box. The roll-press gap between each roll was the total thickness of sum of the Li metal and PTFE film and substrates. For LiF - Li, PTFE film detached with the Li foil as soon as the roll-press process was over for about 30 seconds. In contrast, for the LiF @ C - Li samples, aging was performed for ~ 120 minutes.

LiF - Li and LiF@C - Li characterization Field emission scanning electron microscopy (FE-SEM, JSM-7600F, JEOL, Japan), field emission transmission electron microscopy (FE-TEM, JEM 2100F, JEOL, Japan), and scanning/transmission electron microscopy (S/TEM, Talos F200X, Thermo Fisher Scientific, USA) were employed to determine the surface morphology, crystalline structure, and element mappings of the as-prepared samples. X-ray photoelectron spectra patterns were recorded on a K-alpha XPS system (XPS, theta probe base system, Thermo Fisher Scientific, USA) using a monochromatized Al Ka X-ray as the excitation source. All XPS spectra were collected using the C 1s line at 284.4 eV followed by curve fitting and background subtraction.

Electrochemical property evaluation 2016R coin-type cells were assembled in an argon-filled glove box. For the symmetric cell and Li||LCO full cell tests, 1.3 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 v/v) with 5 wt% fluoroethylene carbonate additive was used as the liquid electrolyte. And, for the Li||NCM full cell test, 1 M $LiPF_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) (1:2:1 v/v) with 10 wt% FEC was used. For plating and stripping morphology evaluation, samples were exposed to a fixed current (0.5 mA cm^{-1}) for 2 hours (1 mAh cm^{-1}). Before SEM evaluation, all samples were washed with DMC to remove the residual salts. For long-term stability test on symmetric cells, a current (1 mA cm^{-1}) was applied for 1 hour during Li plating and stripping processes. For full cell Li||LCO testing, the charge/discharge current density was 3.4 mA cm^{-1} (1C -rate) within the working window of 3.0 to 4.25 V vs. Li^0/Li$^+$. To prepare the LCO cathode, a slurry of LCO (97 wt%), Super-P (1.5 wt%) and poly(vinylidene fluoride) (1.5 wt%) was dispersed in N-methyl-2-pyrrolidone (NMP) solvent. The mass loading of the LCO cathode was about 20 mg cm^{-2} and the density of the electrode was about 5 g cc^{-1}. For full cell Li||NCM-811 test, the charge current density was 1.25 mA cm^{-1} (0.5C - rate) and discharge was 2.5 mA cm^{-1} (1C - rate) within the working window of 3.0 to 4.3 V vs. Li^0/Li$^+$. To prepare the NCM cathode, a slurry of NCM-811 (96 wt%), Super-P (2 wt%) and poly(vinylidene fluoride) (2 wt%) was dispersed in N-methyl-2-pyrrolidone (NMP) solvent. In order to evaluate the full cell under sufficient lithium conditions, 500 micrometer-thick lithium was used, which has an N/P ratio of 30:1 for an LCO cathode and 40:1 for an NCM cathode. A TOSCAT 3000 battery tester (TOSCAT 3000) system was employed to record galvanostatic charge/discharge curves and cycling properties.
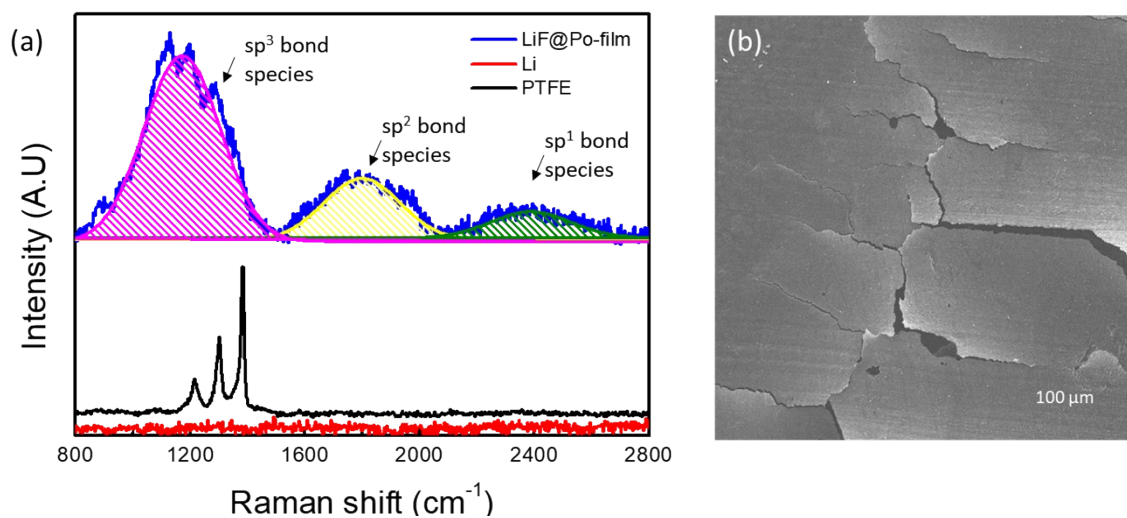
Supplementary figures

Figure S1. Raman spectrum of thick LiF@Po layer which is formed by pressing between PTFE film and Li metal and aging 24 hours for free standing thick film formation. (a) Raman spectrum of bare Li, PTFE film and LiF@Po thick film. The sp^3 (1000-1400 cm^{-1}), sp^2 (1500-2000 cm^{-1}) and sp^1 (2100-2600 cm^{-1}) bond species indicates amorphized PTFE, double and triple carbon-carbon bond, respectively. (b) The SEM image of LiF@Po film after 24 hour reaction time. The free-standing film is formed on Li metal foil, resulting from long time reaction, and the free-standing film is evaluated by Raman spectroscopy after detaching from Li metal.
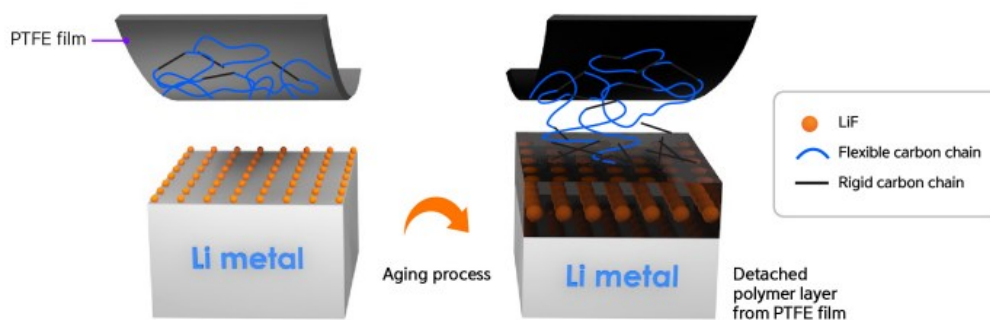
Figure S2. Formation of LiF@Po film on Li metal by pressing with PTFE film and Li metal foil. Initially, LiF nano-particles are formed as soon as lithium reacts with PTFE (within 30s). Subsequently, as the reaction progresses further, partially rigidified carbon chains fall together, forming a composite film of LiF and polymeric carbon chains (LiF@Po).
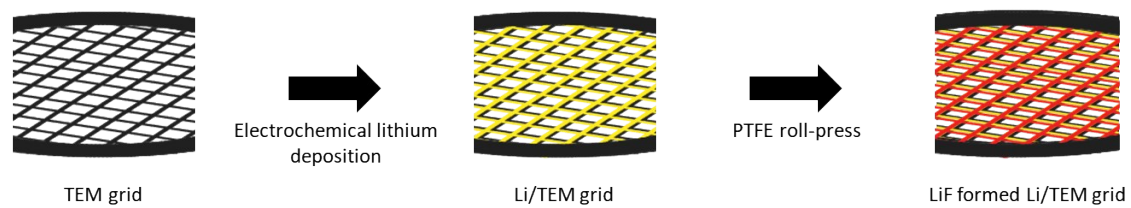
TEM grid   Electrochemical lithium deposition   Li/TEM grid   PTFE roll-press   LiF formed Li/TEM grid

Figure S3. Schematic procedure of LiF@Po-Li formation on a Cu grid for TEM observation. Lithium was deposited at 0.1 mAh cm^{-2} through electrodeposition. The electrolyte was an 1.3M LiPF6 and EC / DEC 3: 7 FEC 5wt%. After the deposition, the grid washed with dimethyl carbonate electrolyte (DMC) was roll-pressed with PTFE to form LiF@Po on the surface.
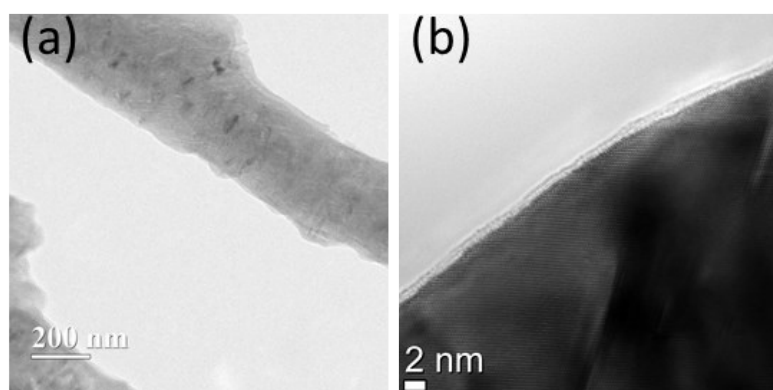
Figure S4. TEM and HR-TEM images deposited Li on Cu grid. (a) Low magnitude TEM image of deposited bare Li by electrochemical deposition on Cu grid. (b) High magnitude HR-TEM image of deposited Li. After washing with DMC several times, thin SEI layer is exist about 1 nm thick. (b) LiF@Po–Li on Cu grid. The orange rectangle shows the crystalline structure of LiF nano particles. (c) The intensity plot of orange rectangle in (b) and the average plane spacing is 2.3 A, corresponding to the (111) plane of LiF
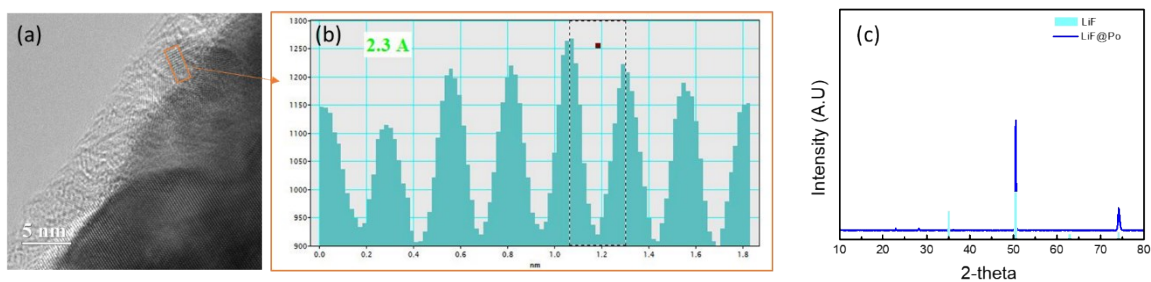
Figure S5. (a-b) HR-TEM images and crystal lattice structure deposited LiF@Po-Li on Cu grid. (a) LiF@Po − Li on Cu grid. The orange rectangle shows the crystalline structure of LiF nano particles. (b) The intensity plot of orange rectangle in (b) and the average plane spacing is 2.3 A, corresponding to the (111) plane of LiF (c) GI-XRD result of LiF@Po layer.
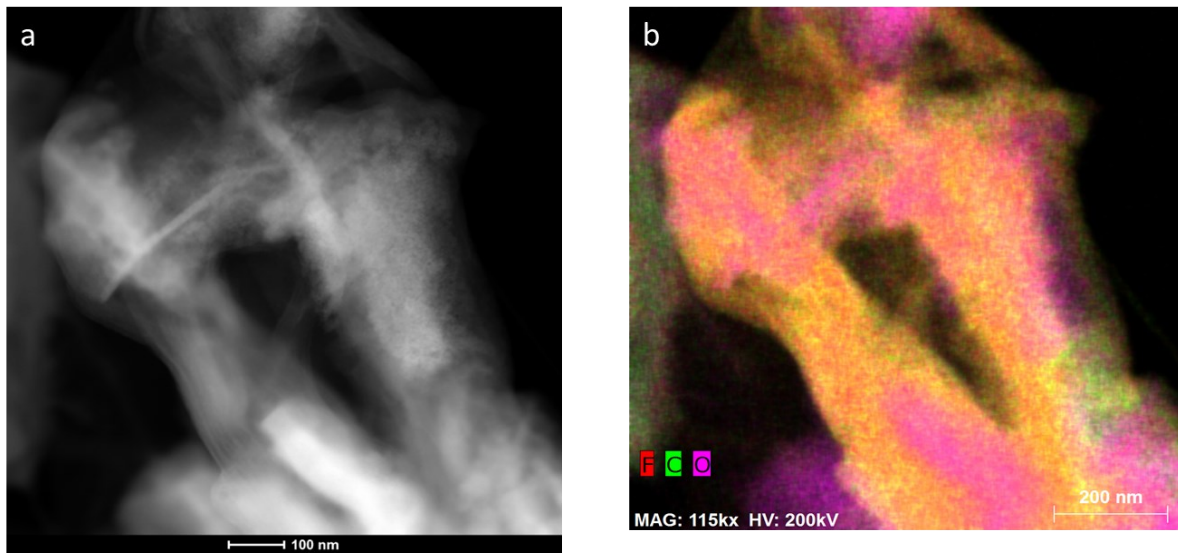
Figure S6. TEM and EDS mapping images of a LiF@Po-coated Li metal surface. (a) TEM image of Li metal deposited on Cu grid. (b) EDS mapping image of (a).
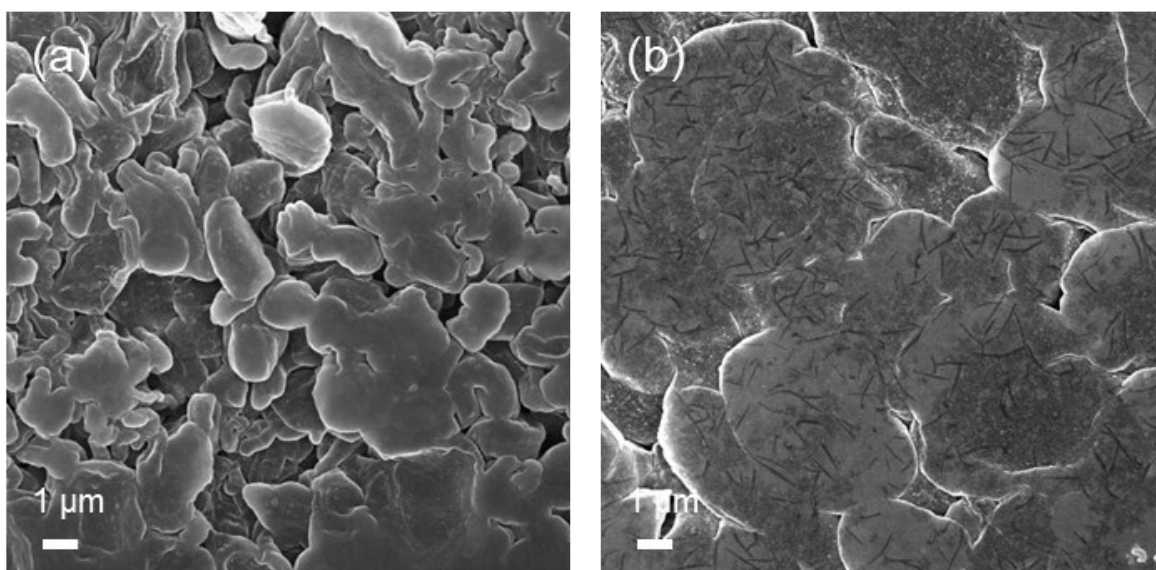
Figure S7. Li plating behavior on LiF@Po coated Li anode of first plating. The different further reaction time (aging) for (a) 30 min and (b) 60 min.
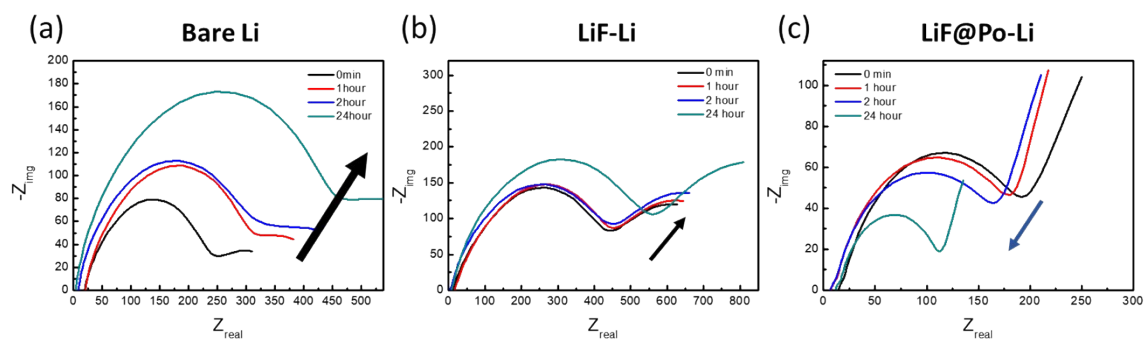
Figure S8. Time dependent EIS spectra of (a) Bare Li, (b) LiF – Li and (c) LiF@Po – Li symmetric cells using $LiPF_6$ 1M in DMC/FEC (4:1 v/v) electrolyte.
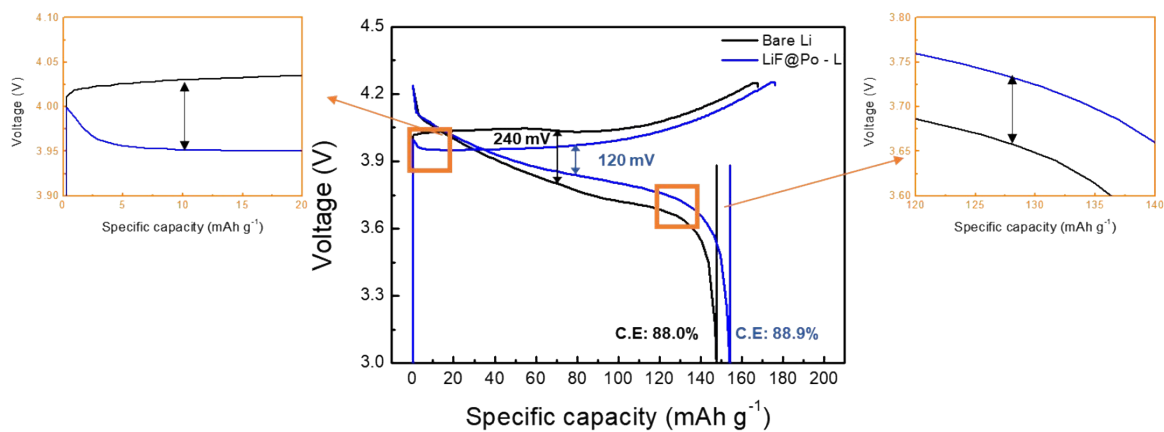
Figure S9. Initial voltage profiles of the Li ‖ LCO and LiF@Po – Li ‖ LCO full cells at 0.1C.
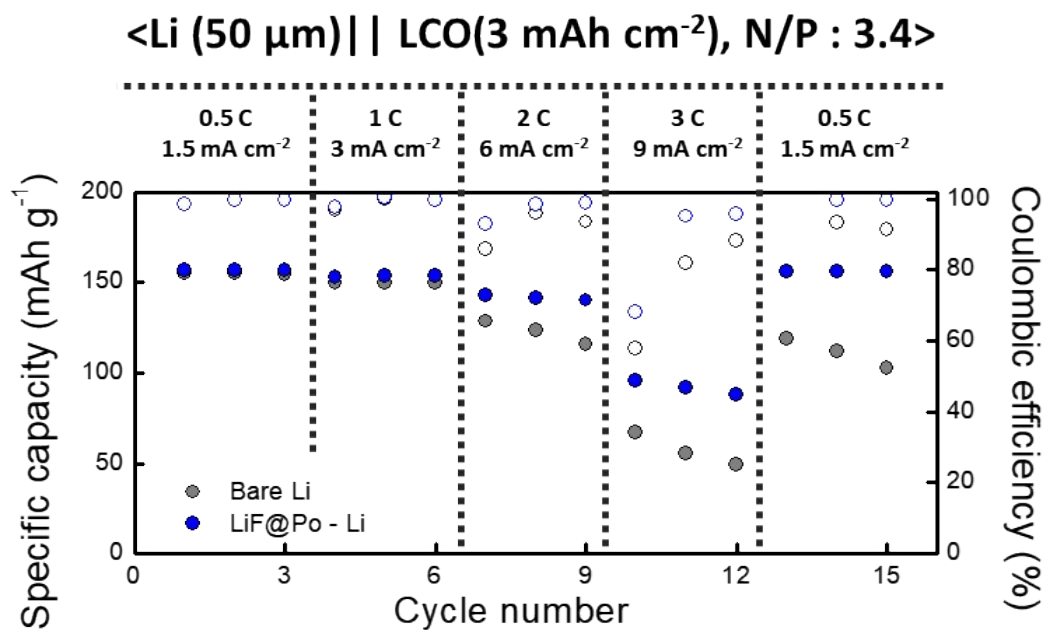
Figure S10. Rate performance of full cells employing bare Li and LiF@Po – Li anodes coupled with LCO cathode with 3 mAh cm^{-2}. 1 M LiPF$_6$ in DMC/FEC (4:1 v/v) was used as the electrolyte. C-rate for discharge was 0.5C (1.5 mA cm^{-2}).
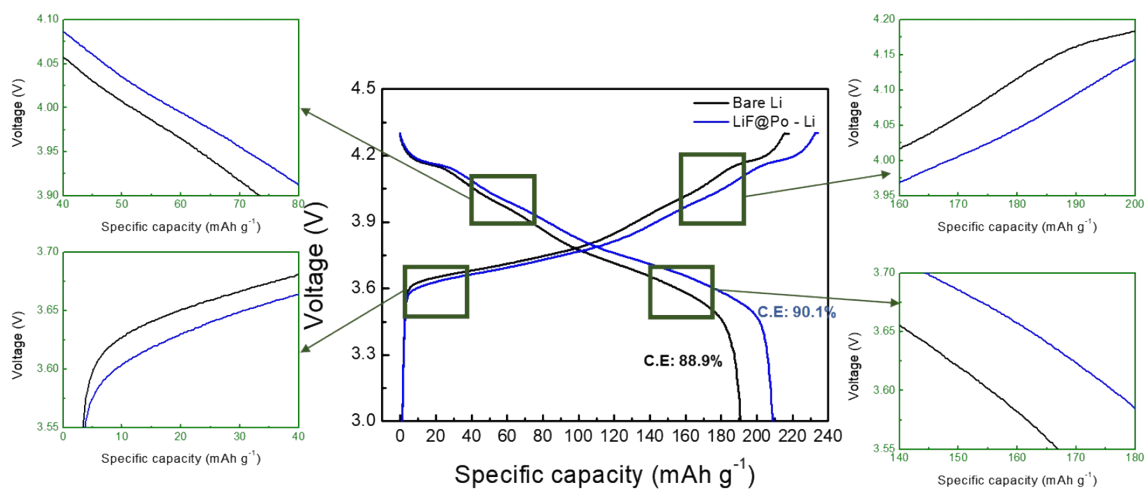
Figure S11. Initial voltage profiles of the Li ‖ NCM and LiF@Po − Li ‖ NCM full cells at 0.1C.
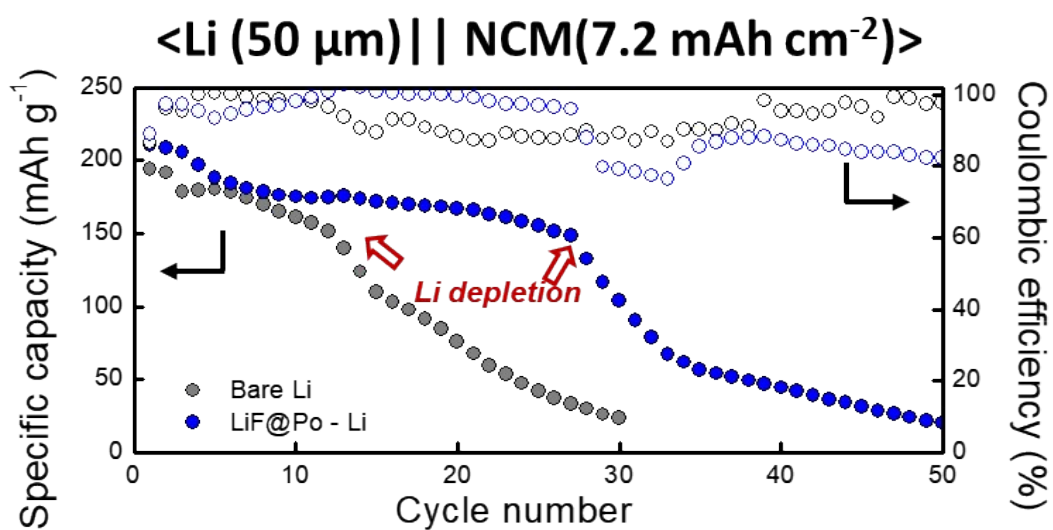
Figure S12. Cycle performances of full cells employing bare Li and LiF@Po – Li anodes coupled with lithium nickel-rich nickel manganese cobalt oxide cathode (NCM 811) cathode with 7.2 mAh cm⁻². 1 M LiPF$_6$ in DMC/FEC (4:1 v/v) was used as the electrolyte. C-rate for charge and discharge was 0.5C (3.6 mA cm⁻²).

Supplementary table 1.: Initial cell properties of full cell (LCO and NCM)

Table S1. The gravimetric specific capacities and Coulombic efficiencies of the full cells employing bare Li and LiF@Po – Li anodes coupled with LCO and NCM cathodes at the first cycle (0.1C)

`	Specific capacity (mAh g⁻¹)	Coulombic efficiency (%)
Li || LCO full cell	147.7	88.0
Li || NCM full cell	192.3	90.1
LiF@Po – Li || LCO full cell	155.7	88.3
LiF@Po – Li || NCM full cell	210.3	90.1

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The Materials Project: A materials genome approach to accelerating materials innovation
APL Materials, 2013, 1(1), 011002.

[2] K.A Persson, Materials Data on LiF (SG:225) by Materials Project, (2016)
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