Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

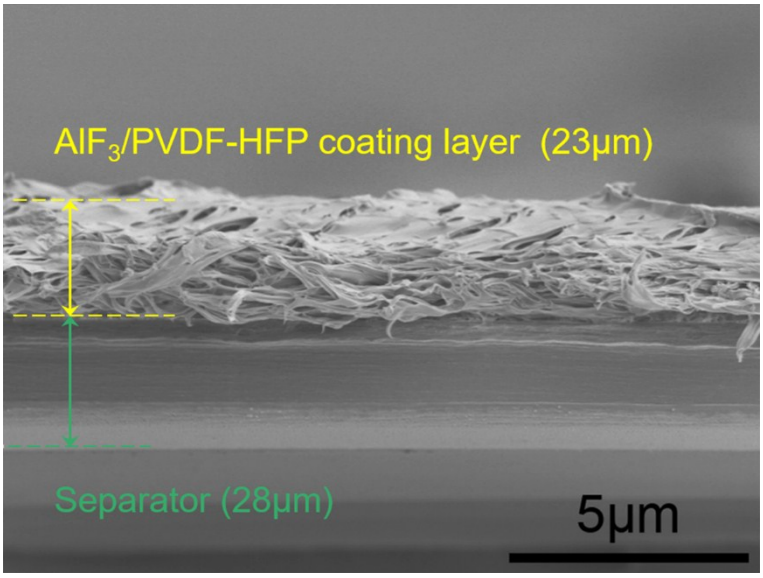

Figure S1. SEM image revealing the thickness of the AlF_3/PVDF-HFP coating and blank separator.

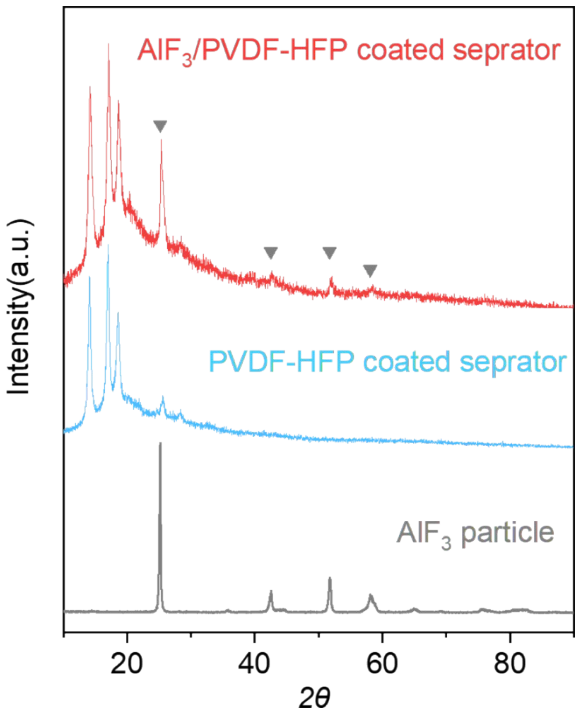

Figure S2. XRD patterns of AlF_3 particles, PVDF-HFP and AlF_3/PVDF-HFP composite coating separators.

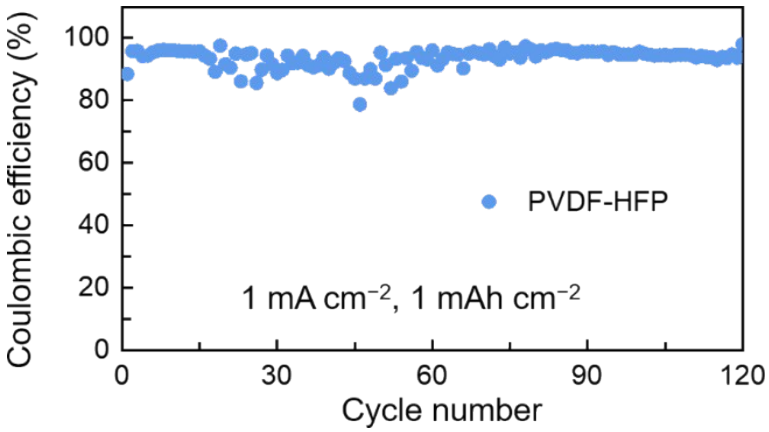

Figure S3. Cycling performances of Li||Cu cell with PVDF-HFP modified separator at 1 mA cm^{-2}. The deposition capacity of Li is fixed at 1 mA h cm^{-2}.

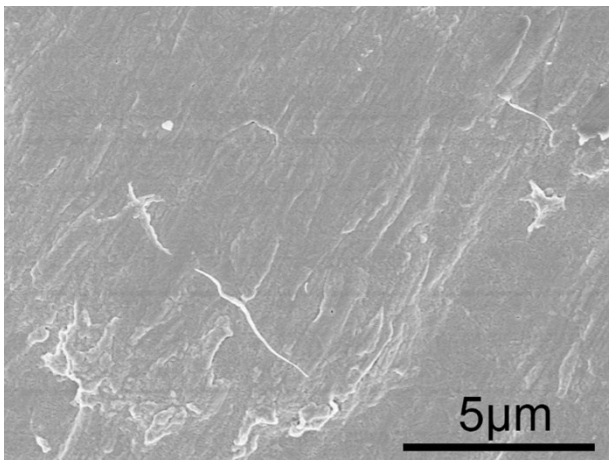

Figure S4. The SEM image of bare Cu substrate.

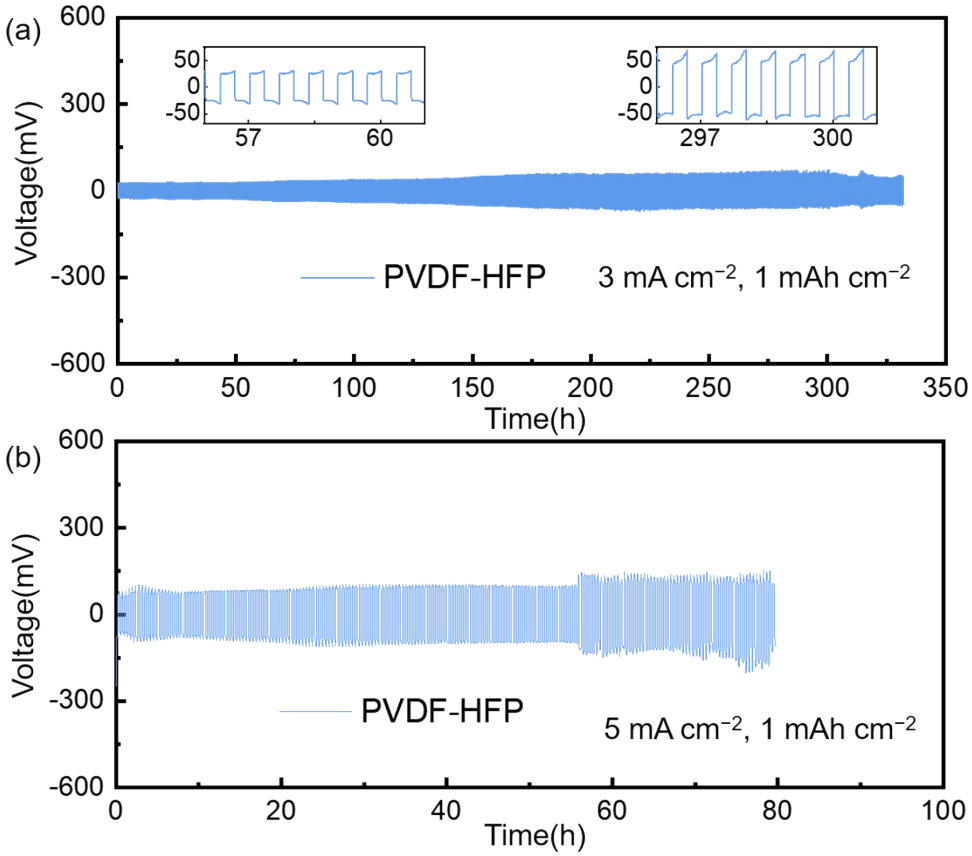

Figure S5. Voltage profiles of the symmetric Li||Li cells with PVDF-HFP modified separator at current density of (b) 3 mA cm^{-2} and (c) 5 mA cm^{-2}. The amount of plated Li is 1 mA h cm^{-2}.

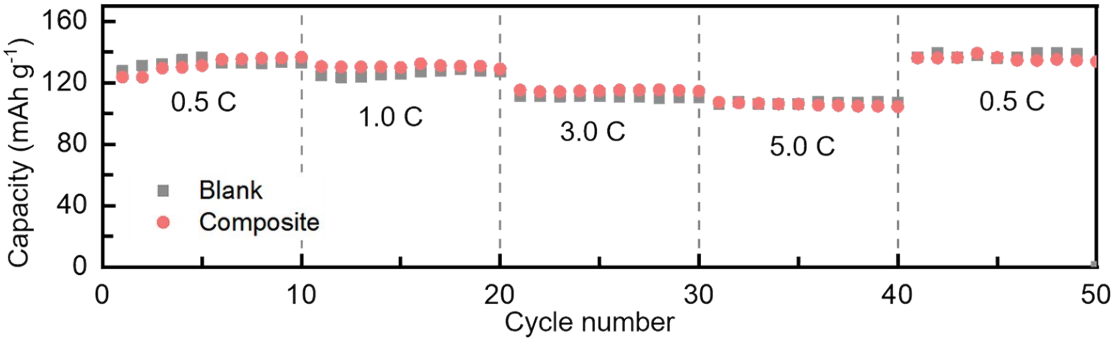

Figure S6. The rate performance of Li||LFO cells with blank and AlF_3/PVDF-HFP composite separators at various current densities from 0.5 to 5 C.

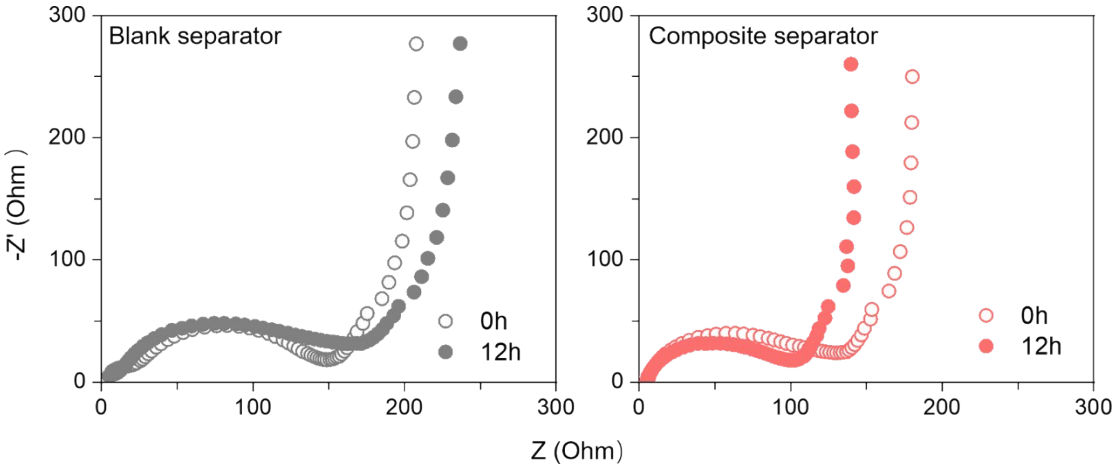

Figure S7. EIS spectra of Li||LFP cells with blank and composite separator before cycling.

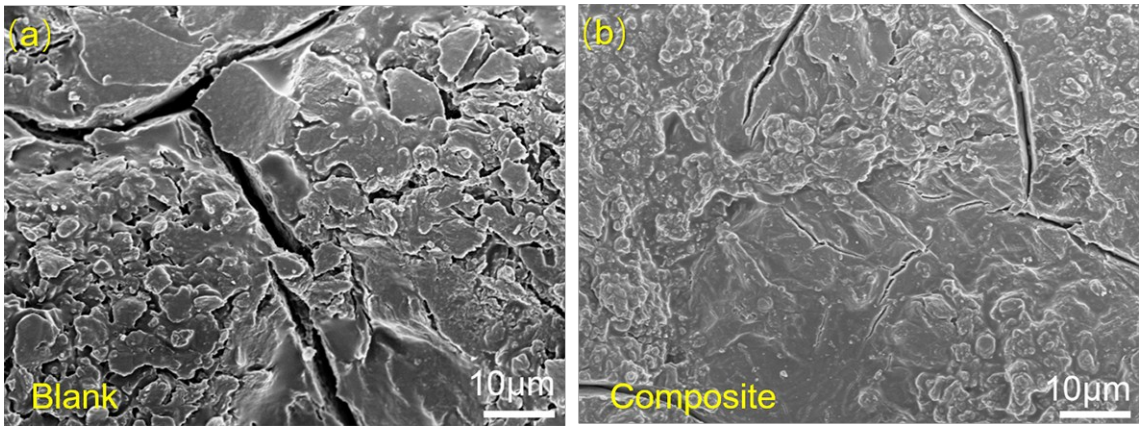

Figure S8. SEM images revealing the morphologies of the Li stripping in the LFP||Li cells with (a) blank and (b) composite separators after the 100th cycle.

Table S1. Compositions of symmetric-cell cycling with different approaches to protect Li metal based on the ether electrolytes

Work	Current density/ mA cm^{-2}	Capacity/ mAh cm^{-2}	Time/h	Ref.
PVDF-HFP@AlF_3 composite separator	3	3	400	This work
	3	1	600	
PVDF-HFP @LiF layer	2	1	200	1
Agarose-modified Cu	2	1	250	2

BN modified hybrid electrolyte	0.1	0.1	300	3
AlI_3-DOL-treated Li	2		~100	4
$MgCl_2$ electrolyte additive	1	1	300	5
Pyr1(12)FSI Ionic liquid Additive	0.5	2	800	6
Liquid-metal-coated Cu foil	0.5	0.5	350	7

Supplementary Reference:

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