

Supplementary Information

An artificial cathode-electrolyte interphase with flame retardant capability enabled by organophosphorus compound for lithium metal batteries

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Table S1. Comparison of similar works on the A-CEI with key features.

CEI thickness	Capacity decrease	Flame retardant property	Reference No.
< 10 nm	13 % on 100 cycles	None	Ref ¹
< 50 nm	16 % on 100 cycles	None	Ref ²
~10 nm	31 % on 100 cycles	None	Ref ³
12 ~ 17 nm	28 % on 100 cycles	None	Ref ⁴
< 10 nm	9.4 % on 100 cycles	Strong (Based on chain reaction inhibition by DMMP)	This work

1 W. Li, D. Cheng, R. Shimizu, Y. Li, W. Yao, G. Raghavendran, M. Zhang and Y. S. Meng, *Energy Storage Mater.*, 2022, **49**, 77–84.

2 T. T. Zuo, F. Walther, S. Ahmed, R. Rueß, J. Hertle, B. Mogwitz, K. Volz and J. Janek, *ACS Energy Lett.*, 2023, **8**, 1322–1329.

3 L. Liu, W. Dai, H. Zhu, Y. Gu, K. Wang, C. Li, C. Pan, M. Zhou and J. Liu, *Nanomaterials*, 2021, **11**, 1–10.

4 I. Moez, D. Susanto, W. Chang, H. D. Lim and K. Y. Chung, *Chem. Eng. J.*, 2021, **425**, 130547.

Table S2. The XPS peak identifications of Ni 2p, Mn 2p, O 1s, C1s, F 1s, and Li 1s with quantifications for the $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) cathode at reference state (REF) and cycled state (x100). The electrochemical cycling was carried out in the voltage range between 2.8 V and 4.3 V with C-rate.

O 1s peak location [REF]	% concentration	Identified composites/species
~529.5 eV	14.33	Lattice oxygen
~531.7 eV	78.22	Surface oxygen (from TM)
~533.9 eV	7.45	Ether oxygen (C-O)
O 1s peak location [NMC811/normal SP x100]	% concentration	Identified composites/species
~529.07 eV	3.30	Lattice oxygen
~531.6 eV	53.44	Surface oxygen (from TM)
~532.4 eV	33.44	Metal carbonate (Li_2CO_3) (* 531.9 can be also metal carbonate)
~533.8 eV	9.81	
O 1s peak location [NMC811/PHDP30 x100]	% concentration	Identified composites/species
~529.1 eV	3.04	Surface oxygen (from TM)
~531.6 eV	90.88	Surface oxygen (from TM)
~533.9 eV	6.08	Ether oxygen (C-O)

C 1s peak location [REF]	% concentration	Identified composites/species
~284.6 eV	61.03	Carbon (calibrated)
~285.9 eV	30.57	-CH from PVDF binder
~290.3 eV	8.41	-CF from PVDF binder
C 1s peak location [NMC811/normal SP x100]	% concentration	Identified composites/species
~284.6 eV	51.33	Carbon (calibrated)
~285.5 eV	38.42	CH from PVDF binder
~290.0 eV	10.25	-CF from PVDF binder
C 1s peak location [NMC811/PHDP30 x100]	% concentration	Identified composites/species

~284.6 eV	50.82	Carbon (calibrated)
~285.6 eV	35.99	CH from PVDF binder
~289.8 eV	13.19	-CF from PVDF binder

F 1s peak location [REF]	% concentration	Identified composites/species
~684.8 eV	14.01	LiF
~687.1 eV	85.99	F from PVDF
F 1s peak location [NMC811/normal SP x100]	% concentration	Identified composites/species
~684.8 eV	50.26	LiF
~686.0 eV	28.26	Li _x PO _y F _z
~687.0 eV	21.48	F from PVDF
F 1s peak location [NMC811/PHDP30 x100]	% concentration	Identified composites/species
~684.9 eV	92.46	LiF
~686.9 eV	7.54	F from PVDF

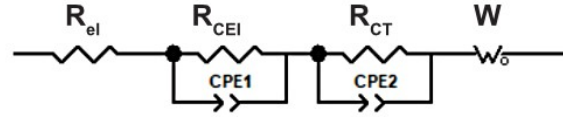
P 2p peak location [NMC811/normal SP x100]	% concentration	Identified composites/species
~130.2 eV	6.95	
~133.7 eV	49.87	Li _x PO _y F _z
~136.9 eV	43.18	-PF from Li _x PF _y
P 2p peak location [NMC811/PHDP30 x100]	% concentration	Identified composites/species
~133.7 eV	67.88	Li _x PO _y F _z (from LiF)
~136.5 eV	32.12	

Li 1s peak location [REF]	% concentration	Identified composites/species
~55.9 eV	100	Metallic Lithium
Li 1s peak location [NMC811/normal SP x100]	% concentration	Identified composites/species
~54.9 eV	8.82	Li ₂ CO ₃
~55.5 eV	73.53	LiF
~56.3 eV	17.65	Li _x PO _y F _z
Li 1s peak location [NMC811/PHDP30 x100]	% concentration	Identified composites/species
~54.3 eV	9.56	Li ₂ CO ₃
~55.6 eV	90.44	Metallic Lithium

Table S3. Thickness data of the cross-sectional observation on the corresponded electrodes in Fig. 4.

Electrode type	Thickest part	Mean thickness
NMC811 (REF)	23.1 μm	20.1 μm
NMC811/normal SP (x100 cycled)	23.5 μm	20.5 μm
NMC811/PHDP30 (x100 cycled)	30.7 μm	28.0 μm

Table S4. EIS fitting results on the Li-metal/Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂ cell and the Li-metal/Li(Ni_{0.8}Mn_{0.1}Co_{0.1})O₂/PHDP30 cell with its equivalent circuit. The cells were cycled in the voltage range of 2.8 – 4.3 V for 100 times with C-rate.



At reference state (REF)

Sample	R_{el} (Ω)	R_{CT} (Ω)
Li-metal/normal SP (REF)	5.9	580.2
Li-metal/PHDP30 (REF)	1.3	454.4

After 100 cycling

Sample	R_{el} (Ω)	R_{CEI} (Ω)	R_{CT} (Ω)
Li-metal/normal SP (x100 cycled)	6.8	32.2	107.3
Li-metal/PHDP30 (x100 cycled)	5.0	19.3	38.9

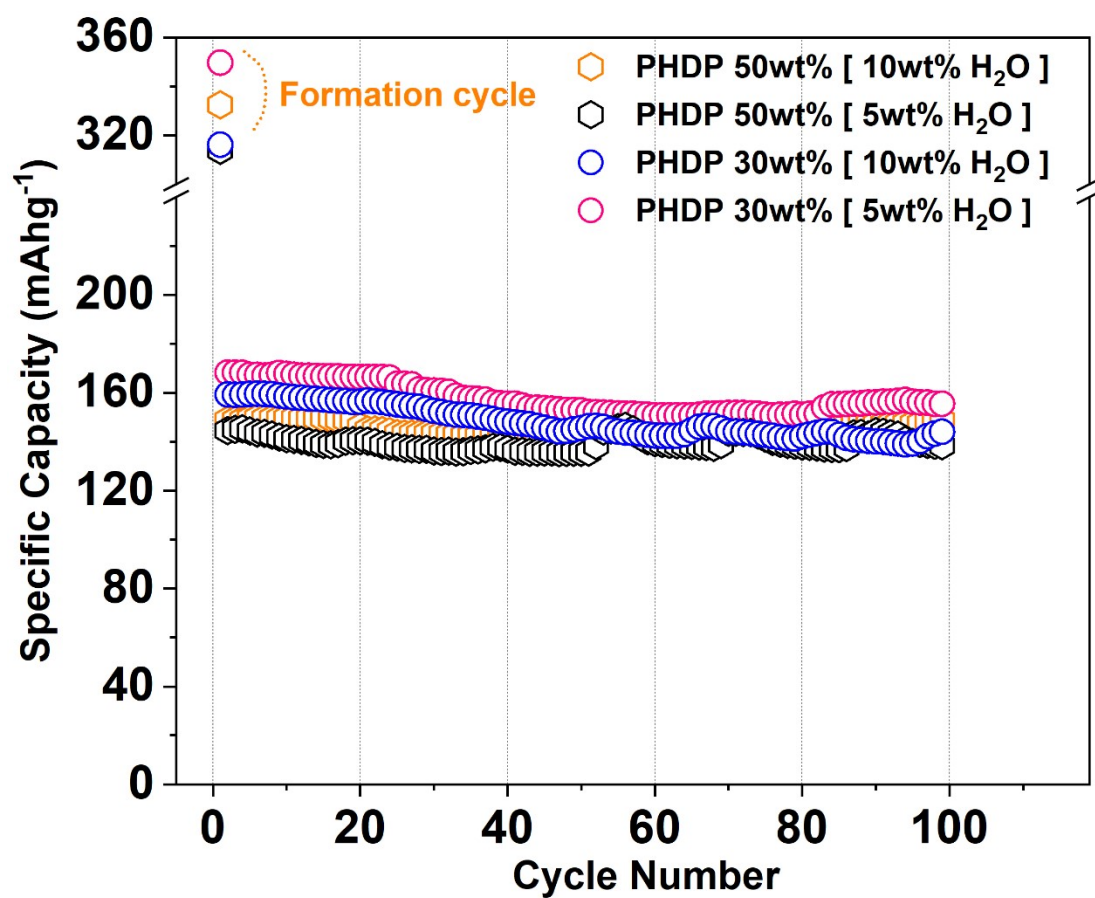


Fig. S1. Comparison of cycling performance between different DMMP concentrations. All cells (Li-metal/ $\text{Li}(\text{Ni}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1})\text{O}_2$) were cycled for 100 times in the voltage range of 2.8 – 4.3 V with C-rate.

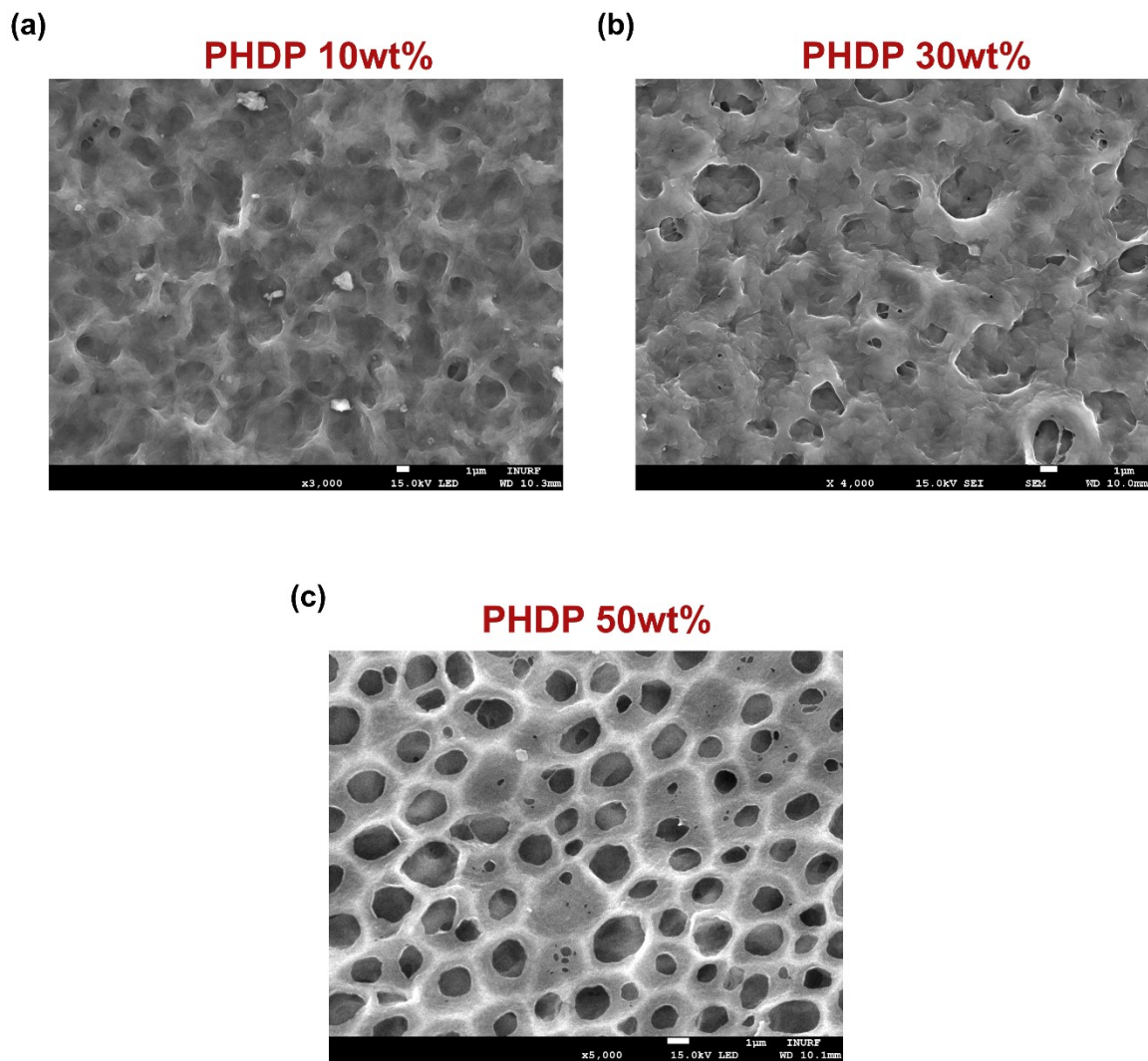
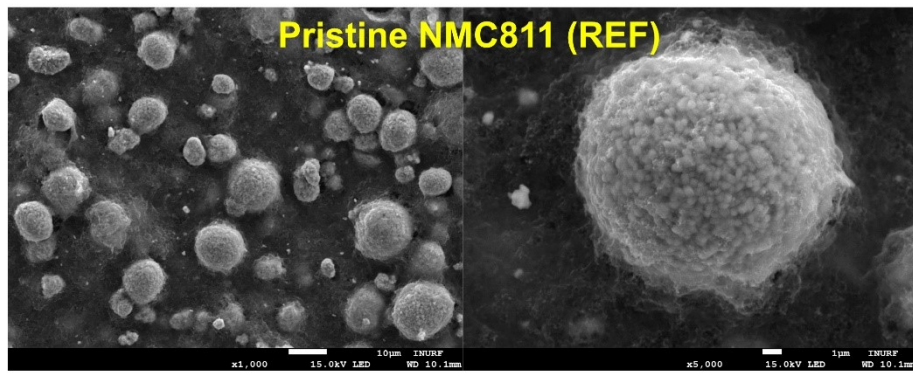
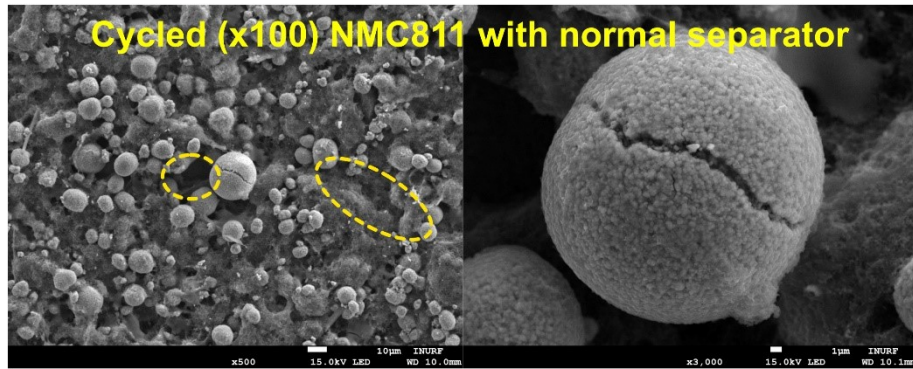


Fig. S2. Porous structure of DMMP(10 wt %)/PVDF-HFP (PHDP 10 wt %), DMMP(30 wt %)/PVDF-HFP (PHDP 30wt%), and DMMP(50 wt %)/PVDF-HFP (PHDP 50 wt %) membranes.

(a)



(b)



(c)

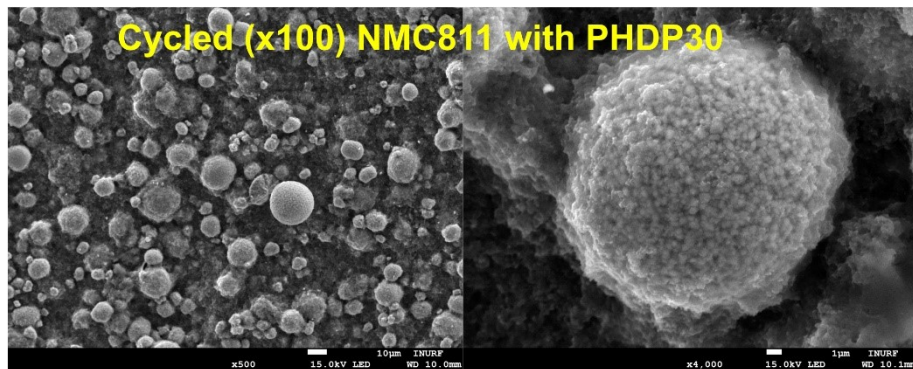
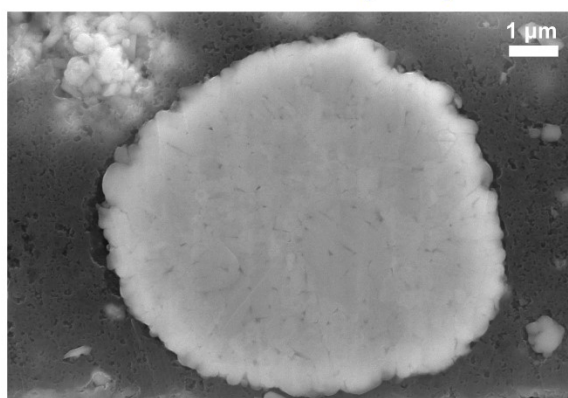
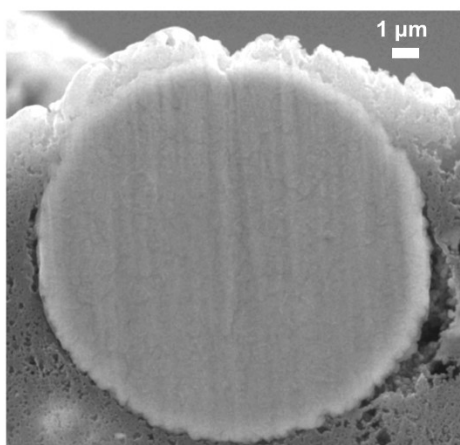


Fig. S3. Surface morphology of (a) pristine NMC811, (b) NMC811 cathode with polypropylene separator, and (c) with the PHDP30 A-CEI cycled for 100 times (x100) in the voltage range between 2.8 V and 4.3 V at C-rate.

(a) **Pristine state (REF)**



(b) **X100 cycling with PHDP30 (A-CEI)**



(c) **X100 cycling with normal SEP (PP)**

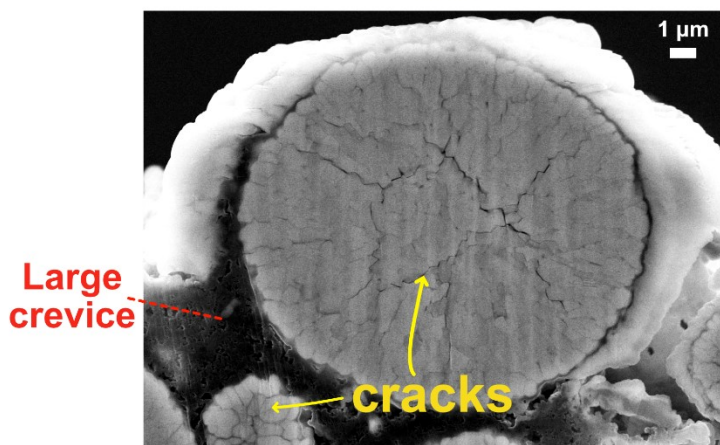


Fig. S4. Comparison of the cross-section of the NMC811 cathode material with high SEM magnification between (a) pristine state (REF), (b) with A-CEI cycled for 100 times, and (c) with the normal polypropylene (PP) separator cycled for 100 times.

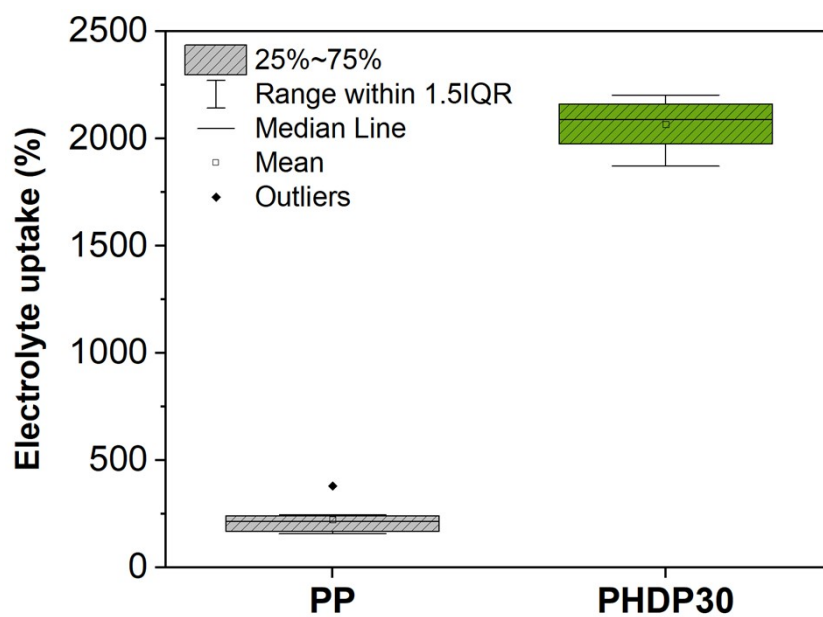


Fig. S5. Electrolyte uptake comparison between commercially available polypropylene (PP) separator and the PHD30 A-CEI.

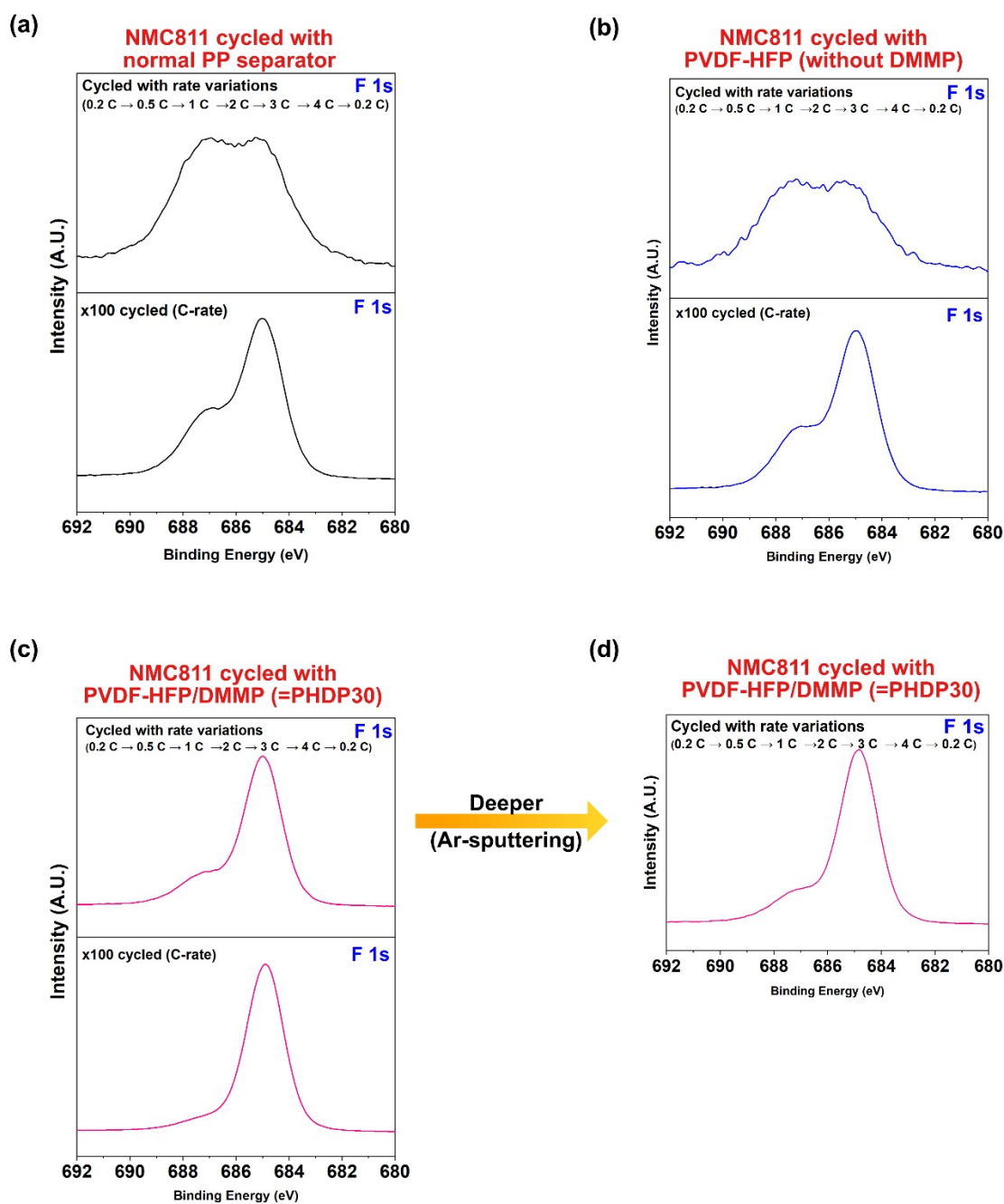


Fig. S6. F 1s XPS spectra on (a) NMC811 cathode cycled with normal polypropylene (PP) separator with rate variations (0.2 C, 0.5 C, 1 C, 2 C, 3 C, 4 C, and back to 0.2 C) and constant rate (C-rate) in the voltage range of 2.8 – 4.3 V. F 1s XPS spectra on (b) NMC811 cathode cycled with PVDF-HFP membrane with the rate variations and constant rate (C-rate) in the voltage range of 2.8 – 4.3 V. The PVDF-HFP membrane functions as a separator, and was synthesized as the identical method used for PHDP30 A-CEI. (c) F 1s XPS spectra on (b) NMC811 cathode cycled with PVDF-HFP/DMMP (=PHDP30 A-CEI) with the rate variations and constant rate (C-rate) in the voltage range of 2.8 – 4.3 V. (d) F 1s XPS spectra in a deeper location on NMC811 cathode cycled with PVDF-HFP/DMMP (=PHDP30 A-CEI) with the rate variations. 1 keV Ar⁺ primary beam with a diameter of 300 mm was employed for the Ar-sputtering (time: 60 sec).

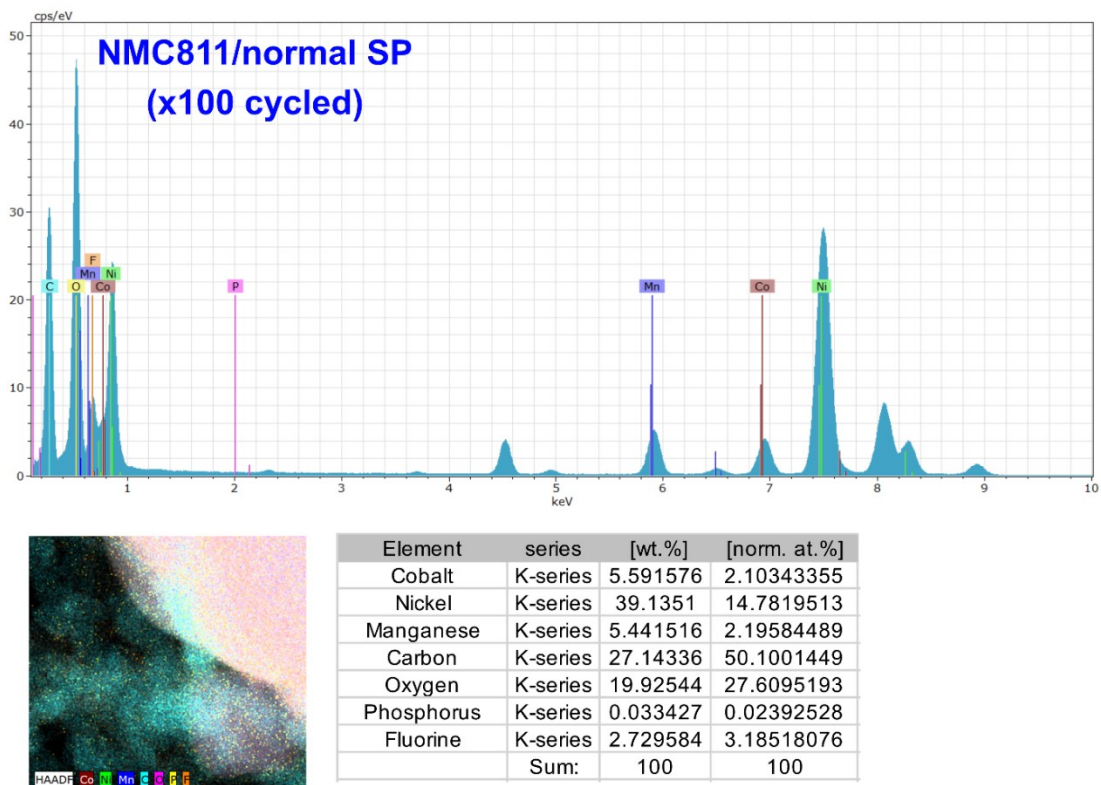


Fig. S7. TEM-EDS analyses of the NMC811 particle with normal separator cycled for 100 times in the voltage range between 2.8 V and 4.3 V at C-rate.

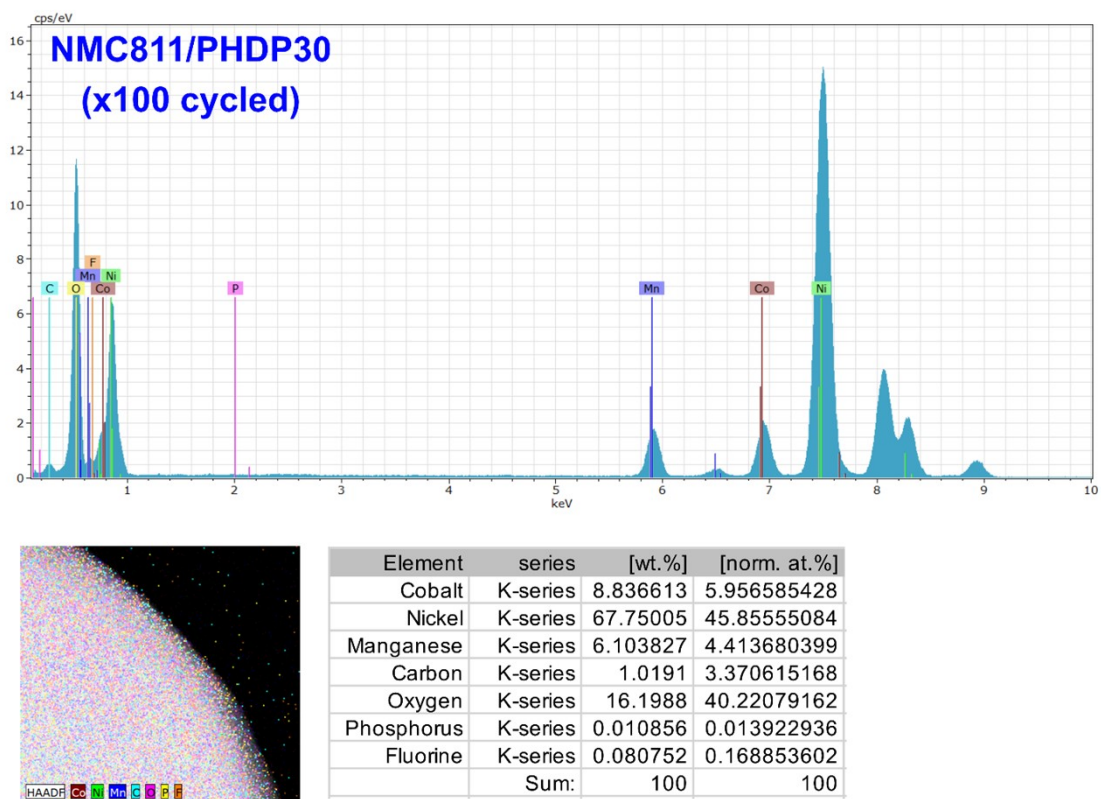


Fig. S8. TEM-EDS analyses of the NMC811 particle with PHDP30 cycled for 100 times in the voltage range between 2.8 V and 4.3 V at C-rate.

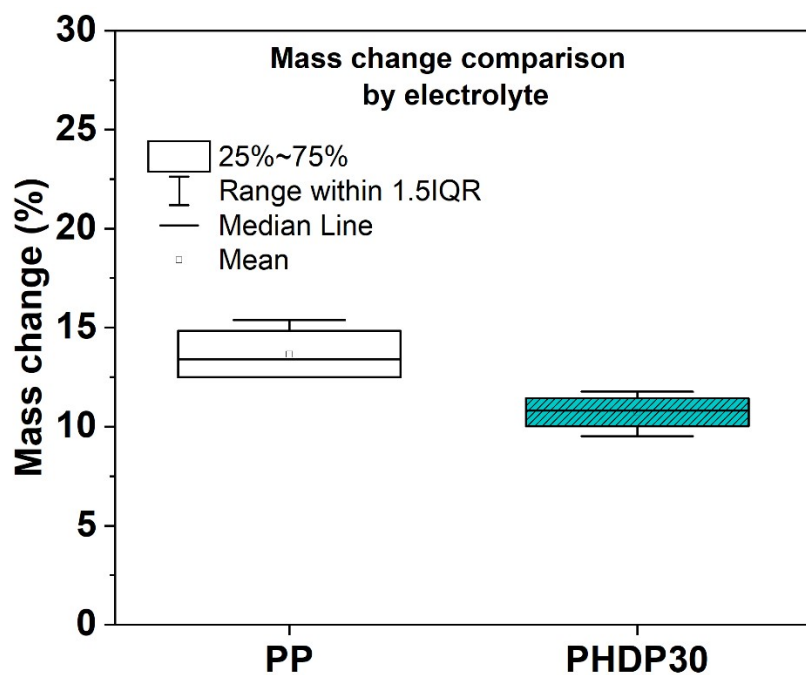


Fig. S9. Mass change comparison by electrolyte (LiPF₆ in(EC:EMC=50:50 (v/v)) between the polypropylene (PP) separator and the A-CEI (=PHDP30).

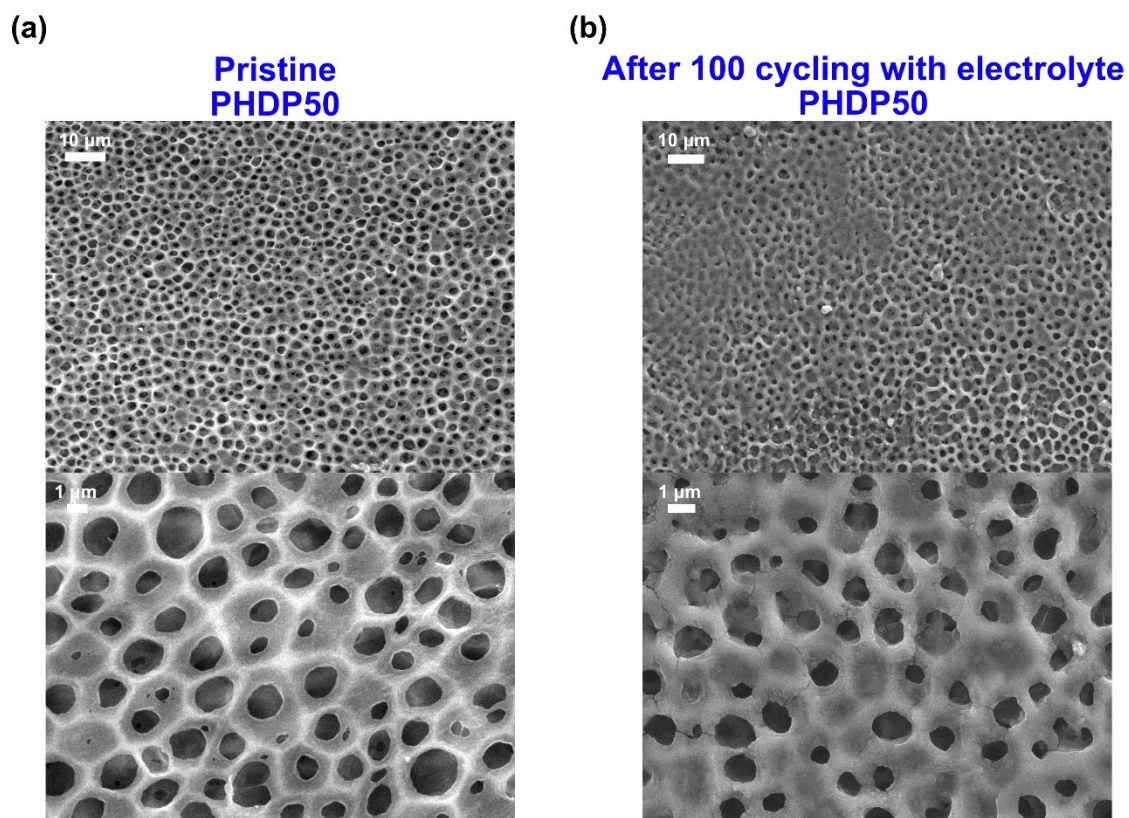


Fig. S10. Comparison of the membrane structure between (a) the pristine PHDP50 (50 wt % DMMP/10 wt % PVDF-HFP matrix) and (b) the cycled PHDP50 with the electrolyte for 100 times in the voltage range of 2.8 – 4.3 V (C-rate).

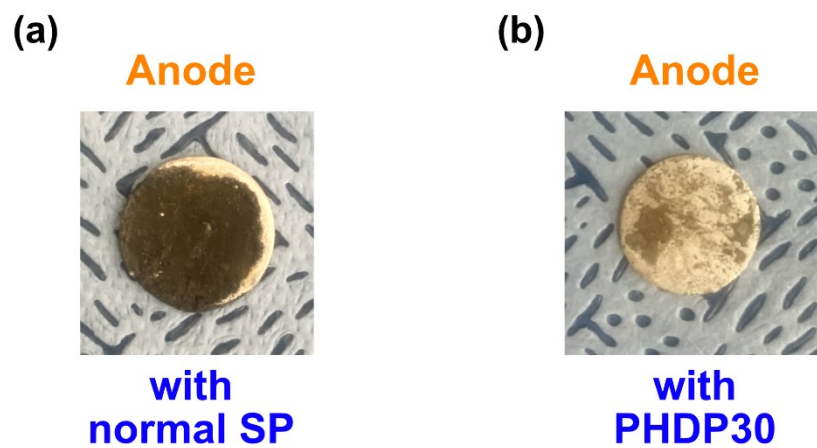


Fig. S11. Comparison on the lithium dendrite growth at anode between the lithium metal cell cycled with (a) normal separator (normal SP) and (b) with the A-CEI (PHDP30). The electrochemical cells were cycled for 100 times in the voltage range of 2.8 – 4.3 V at C-rate.