Supporting Information

Hybrid Poly(ionic liquid)/Polyhedral Oligomeric Silsesquioxane Artificial Solid Electrolyte Interphase for Lithium Metal Batteries

Wei-Ting Chou[a], Thi-Ngoc Pham[a], Ta-Ching Yang[a], Yun-Jie Tsai[a], Hsisheng Teng[a] and Jeng-Shiung Jan[a,b]*

[a] Department of Chemical Engineering, National Cheng Kung University, Tainan 70101, Taiwan

[b] Program on Smart and Sustainable Manufacturing, Academy of Innovative Semiconductor and Sustainable Manufacturing, National Cheng Kung University, Tainan, 70101, Taiwan

[*]Correspondence: Jeng-Shiung Jan, Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, Phone: +886-6-2757575 ext. 62660. Fax: +886-6-2757575.

AUTHOR EMAIL ADDRESS: jsjan@mail.ncku.edu.tw

Table S1. Calculation results of CV test

	$I_{p,a}$ (Ma)	$I_{p,c}$ (Ma)	$I_{p,a}/I_{p,c}$	Q_a (C)	Q_c (C)	Q_a/Q_c
VC12	0.94	0.74	**1.27**	1.166	1.136	**1.03**
VP200	1.29	0.92	**1.40**	1.73	1.67	**1.04**

Table S2 Fitted values of EIS test

Resistance (Ω)	Bare Li			VC12			VP200		
	R_b	R_{SEI}	R_{ct}	R_b	R_{SEI}	R_{ct}	R_b	R_{SEI}	R_{ct}
activation	2.56	**69.45**	118	1.68	**32.29**	164.6	2.98	**20.14**	158.6
20th cycle	1.65	**80.83**	205.3	1.67	**18.87**	88.33	2.01	**38.43**	245.5
40th cycle	1.59	**72.95**	231	1.80	**18.61**	97.44	2.62	**94.47**	200.1
60th cycle	2.27	**81.53**	186.9	4.21	**12.75**	117.4	2.36	**84.36**	189.8
80th cycle	2.16	**94.88**	232.1	1.94	**26.07**	110.3	3.16	**88.61**	206.2
100th cycle	1.96	**106.4**	308.7	2.43	**29.93**	120	3.55	**85.78**	173.7
150th cycle	2.11	**108.6**	215.3	2.56	**44.31**	121	17.86	**106.1**	169.5
200th cycle	1.58	**111.7**	170.3	3.55	**70.83**	170.4	4.21	**123.1**	171
250th cycle	1.42	**149.6**	176.4	3.12	**47.53**	165.2	4.14	**131.2**	169.5

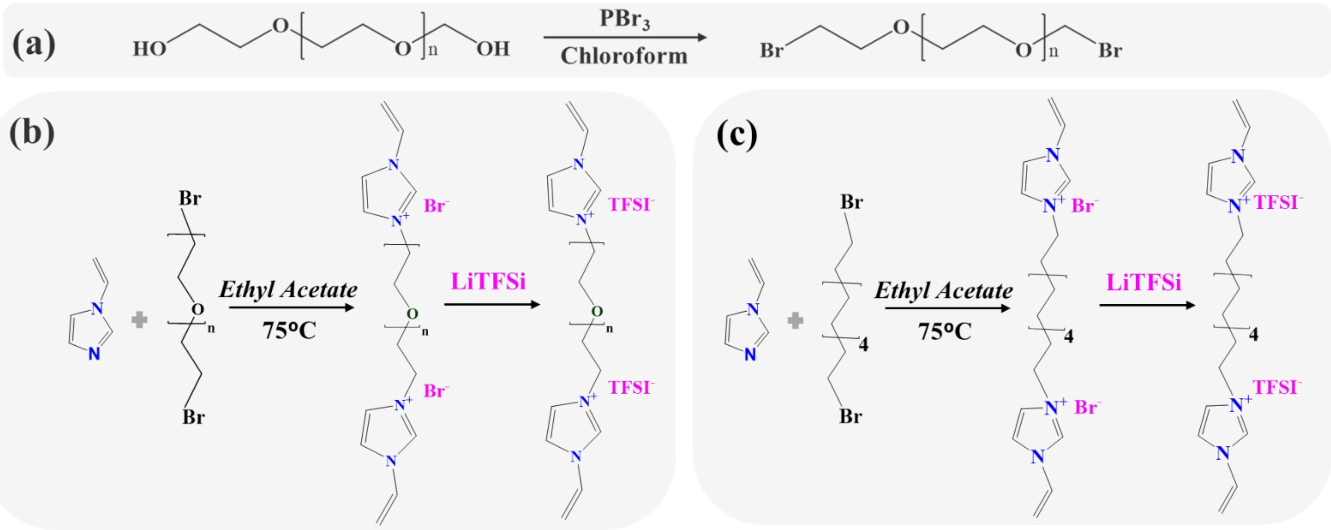
Table S3 Lithium-ion transference number (T_{Li^+}) calculated for VC12 and VP200

	I_0 (μA)	I_s (μA)	R_0 (Ω)	R_s (Ω)	t_{Li+}
VC12	25.7	22.2	276.06	268.07	**0.62**
VP200	58.8	50.2	142.98	153.34	**0.59**

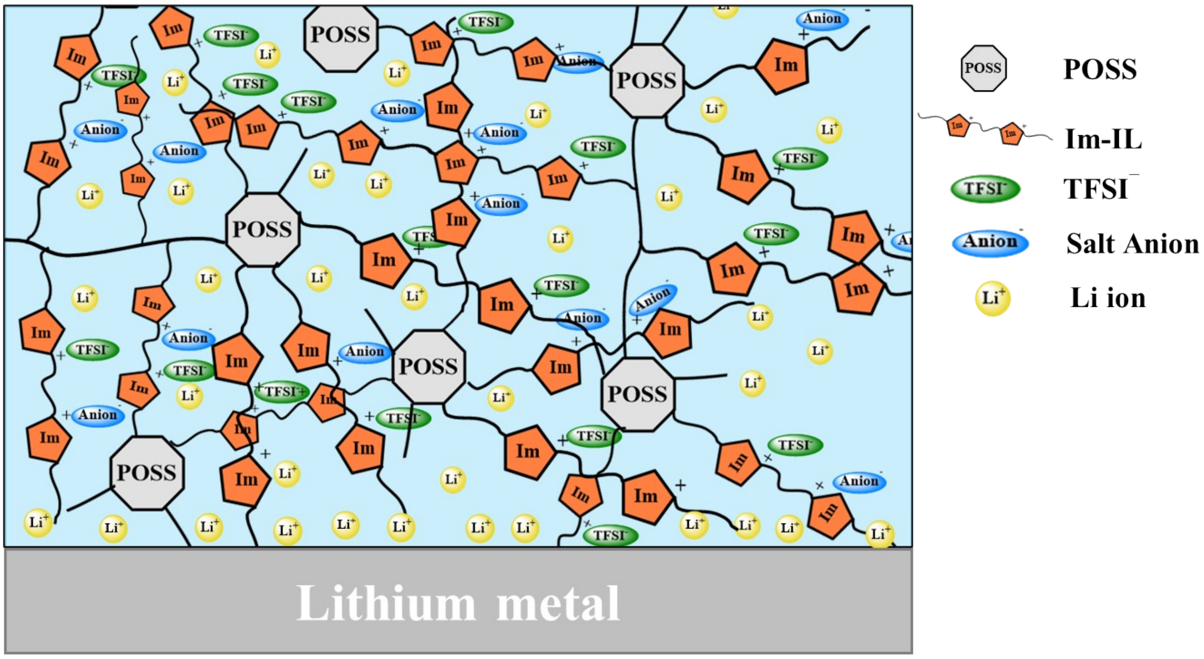
Table S4 Comparison of this work with the reported artificial SEI layer for the Li anode

Materials	Electrode	Electrolyte	Test Conditions	Capacity Retention (%)	Ref.
Organic/inorganic hybrid of PILs with POSS polymer	Im-IL/POSS@Li|LFP (VC12)	1M $LiPF_6$, EC:DEC (1/1, v/v) 1M LiTFSI, DOL:DME (1/1, v/v) with 2% $LiNO_3$	1C 1C	94.7 (500 cycles) 84.6 (1000 cycles) 99.6 (200 cycles) 70.8 (500 cycles)	**This work**
Li_2O/Li_2Se artificial layer	LOSe-NA@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v) with 1% $LiNO_3$	1C	80 (290 cycles)	1
Organic fluorinated siloxane and inorganic LiF	PMTFPS@Li|LFP	0.6 M LiTFSI, DOL/DME (1:1 v/v) with 0.4 M $LiNO_3$	1C	90.1 (400 cycles)	2
LiZn alloy and PEO polymer	LZP@Li|LFP	1.0 M $LiPF_6$, EC: DEC (1:1, v/v) with 5 vol% FEC	1C	82.2 (200 cycles)	3
LiF- and nano-Ag-enriched hybrid layer	LNA@Li|LFP	1M $LiPF_6$, EC: EMC: FEC (3:7:1, v/v)	0.5 mA/cm^2	90.4 (400 cycles)	4
PSA-based artificial SEI layer	70cPSA@Li|LFP	1M $LiPF_6$, EC:DEC (1/1, v/v)	1C	93 (250 cycles)	5
LiF-Rich Interfacial Protective Layer	LiF@Li|LFP	1M $LiPF_6$, EC:DEC (1/1, v/v)	0.5C	91.5 (200 cycles)	6
In situ reaction PAA and SnF_2	PAA-SnF_2@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v) with 2% $LiNO_3$	1C	88.6 (350 cycles)	7
Organic–inorganic hybrid POSS-LiBMAB	POSS-LiBMAB@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v) with 2% $LiNO_3$	1C	70.8 (560 cycles)	8
LPEDV artificial SEI layer	LPEDV@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v)	1C	98.2 (400 cycles)	9
$[LiNBH]_n$ artificial SEI layer	$[LiNBH]_n$@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v) with 1% $LiNO_3$	1C	98.6 (200 cycles)	10
Organic LiSFSI-PET4A-PETMP	LFPP@Li|LFP	1M $LiPF_6$, EC:DMC:DEC (1/1/1, v/v/v)	1C	88.6 (200 cycles)	11
Organic green LiPLA layer	LiPLA@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v) with 2% $LiNO_3$	0.5C	98 (200 cycles)	12

Material	Electrode	Electrolyte	Test Conditions	Capacity Retention (%)	Ref.
Organic LiBAMB-PETMP (LP) layer	LP@Li|LFP	1M LiTFSI, DOL:DME (1/1, v/v)	1C	87.2 (300 cycles)	13
Li_2S interfacial layers	Li_2S@Li|LFP	1M $LiPF_6$, EC:DEC (1/1, v/v) with 5wt% FEC	0.5C	80 (120 cycles)	14
organic/inorganic LLN coating	LLN@Li|LFP	1M $LiPF_6$, EC:DEC (1/1, v/v)	1C	87.4 (150 cycles)	15
Organic/inorganic PVDF-HFP & LiF	APL@Li|LFP	1M $LiPF_6$, EC:DEC (1/1, v/v)	0.5C	80 (250 cycles)	16
High-polarity PVDF coating layer	δ-PVDF@Li|LFP	1.2M $LiPF_6$, EC:DEC (1/2, v/v) with 4wt% FEC	0.5C	94.3 (200 cycles)	17
Self-adapting SEI layer	LiPAA@Li|LFP	1M $LiPF_6$, EC:DMC:DEC (1/1/1, v/v/v)	0.5C	86.7 (500 cycles)	18
organic/inorganic PECA layer	Li(PECA+$LiNO_3$)|LFP	1M $LiPF_6$, EC:DMC (1/1, v/v)	1C 2C	97 (150 cycles) 93 (500 cycles)	19



Scheme S1. Scheme of the preparation of (a) Br-PEG200-Br, (b) [VIm-PEG200-VIm][TFSI], and (c) [VIm-C12-VIm][TFSI].



Scheme S2. Schematic illustration of PIL-POSS ASEI mechanism: Li^+ conduction and anion regulation.

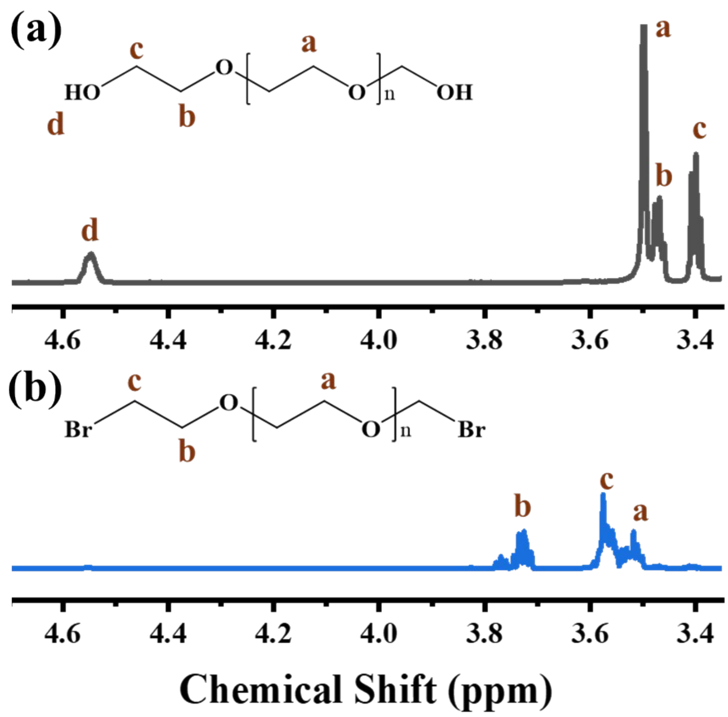


Fig. S1 ^{1}H NMR spectra of (a) PEG_{200} and (b) Br-PEG_{200}-Br in d_6-DMSO.

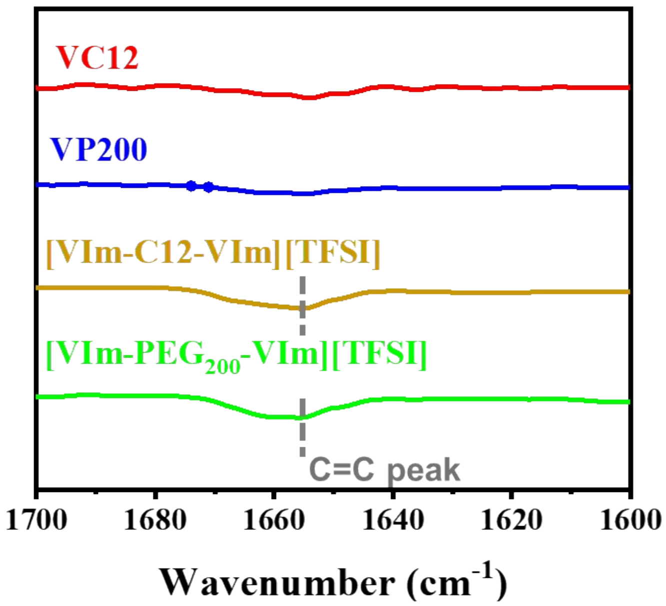


Fig. S2 FT-IR spectra of the ASEI precursors VC12, VP200, [VIm-C12-VIm][TFSI], and [VIm-PEG200-VIm][TFSI].

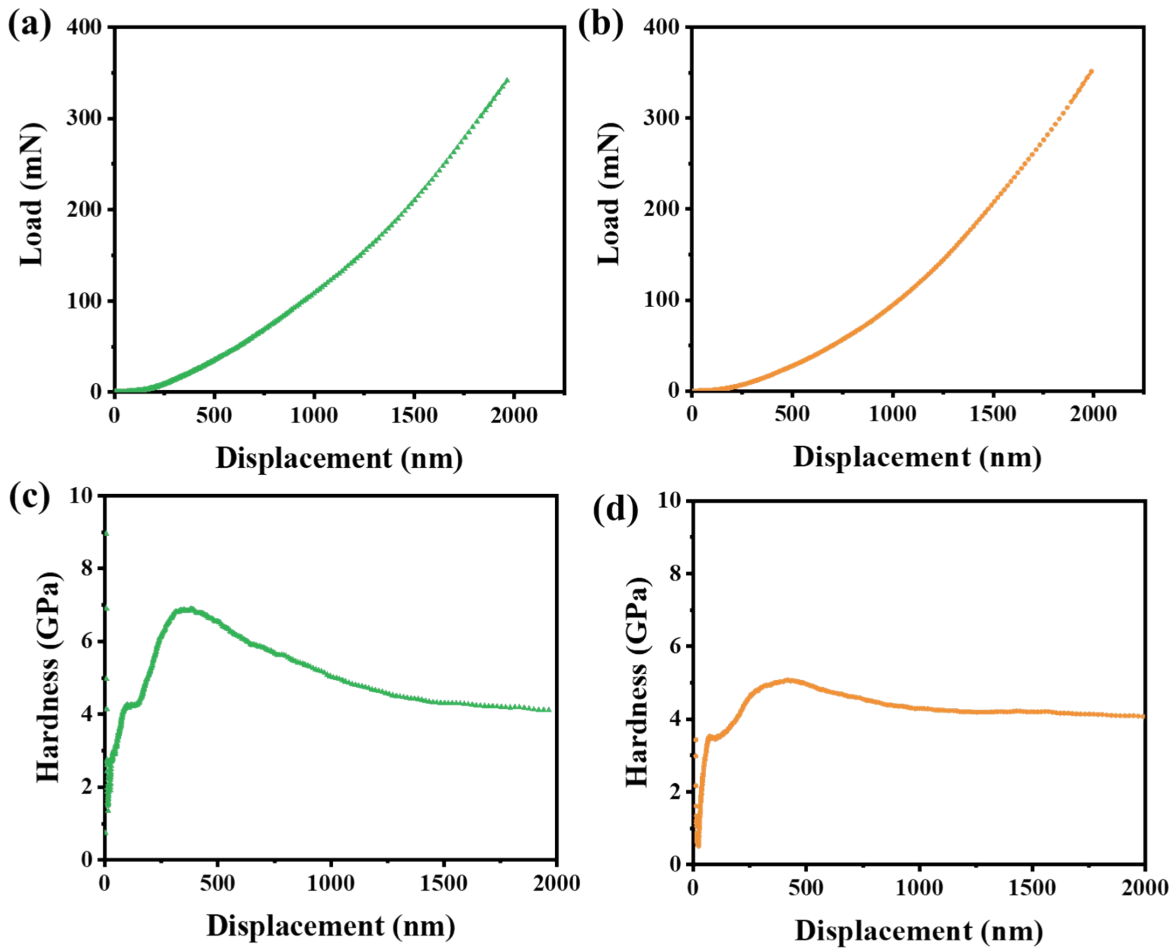


Fig. S3 (a) Load-displacement curves for VC12 and (b) VP200; (c) Hardness versus indentation depth curves for VC12 and (d) VP200.

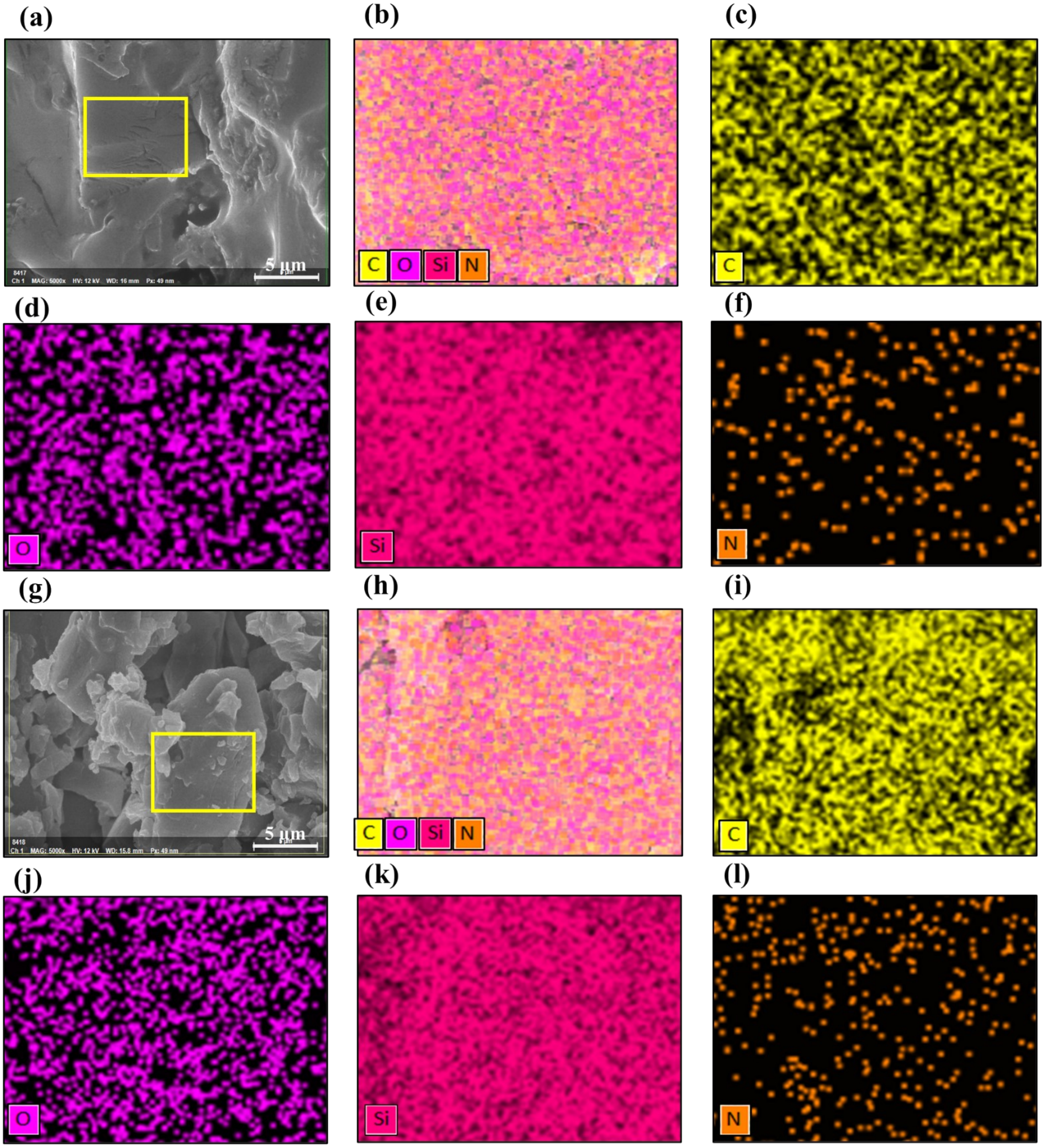


Fig. S4 SEM images and corresponding EDS elemental mapping of the hybrid Im-IL/POSS materials: (a–f) VC12 and (g–l) VP200.

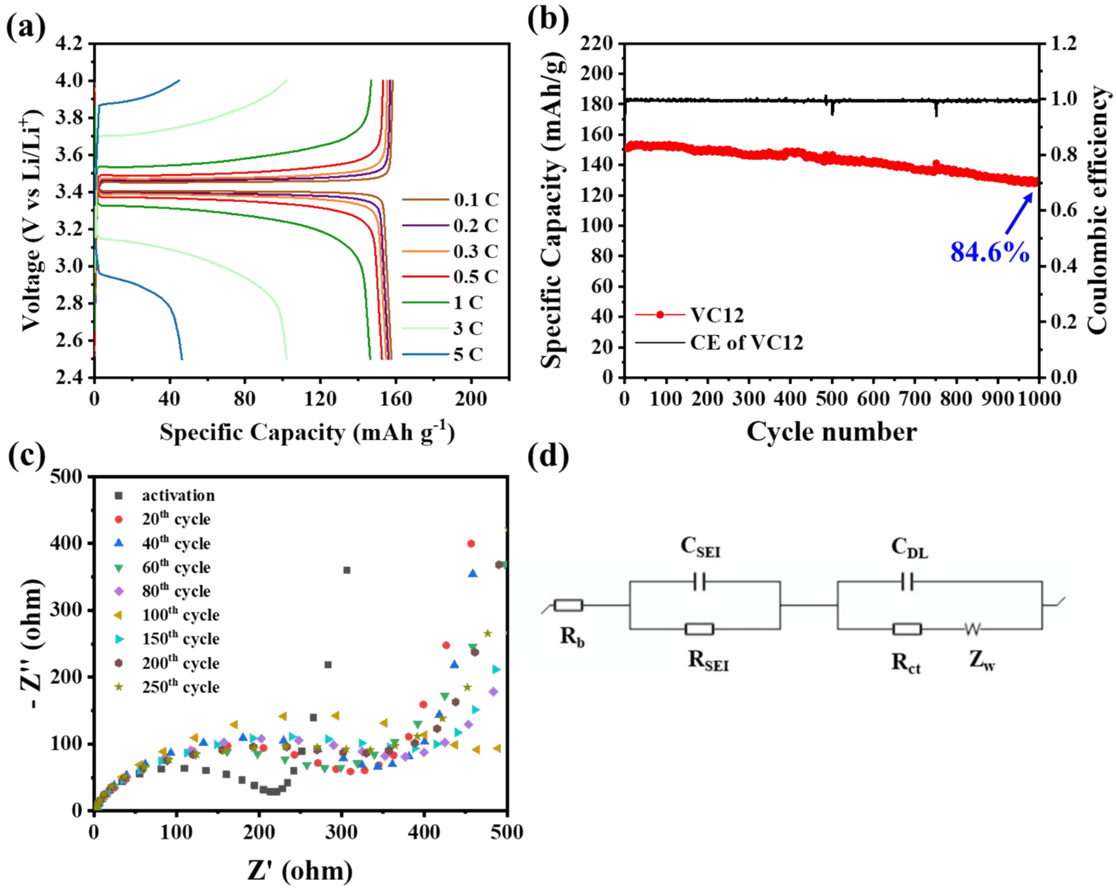


Fig. S5 (a) Charge-discharge curves of Li|LFP cells, (b) Cycling performance of VC12@Li|LFP at 1C after 1000 cycles, (c) EIS profiles of Li|LFP cells, and (d) The appropriate equivalent circuit employed to fit data.

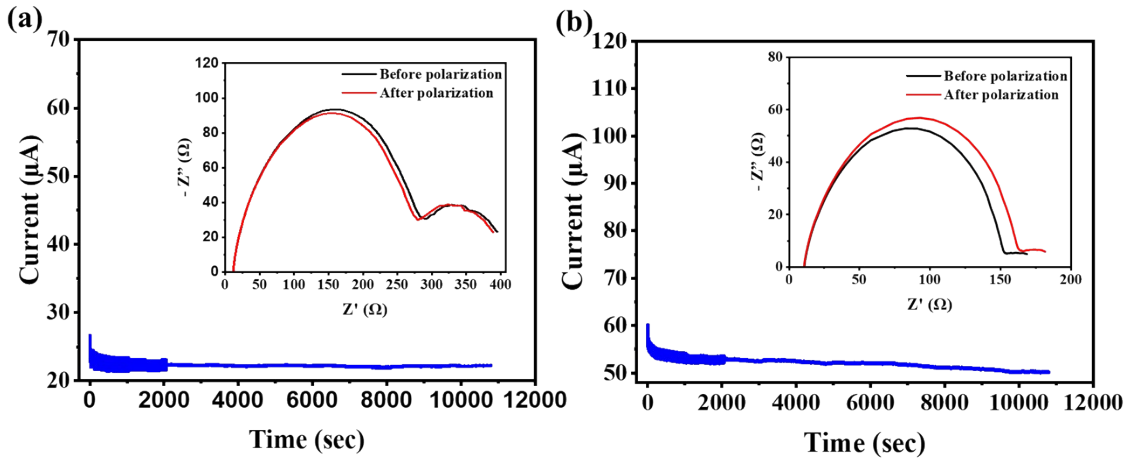


Fig. S6 Lithium transference number of (a) VC12@Li|electrolyte| VC12@Li and (b) VP200@Li|electrolyte| VP200@Li cells.

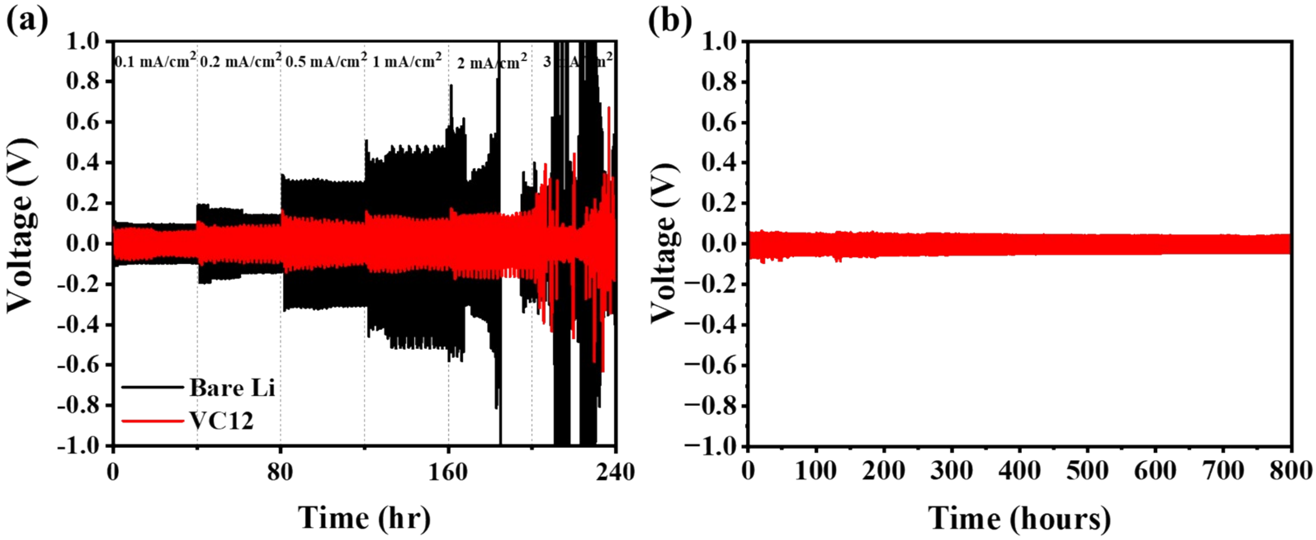


Fig. S7 (a) Voltage-time profiles of symmetric cells with Li|LFP and VC12@Li|LFP cells and (b) Long-term cycling stability of the symmetric VC12@Li|VC12@Li cell at 0.5 mA cm^{-2}.

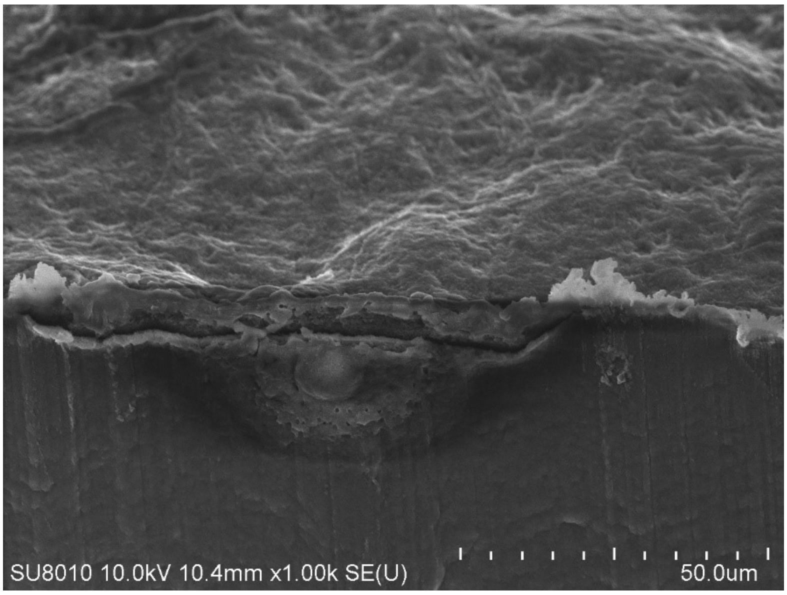


Fig. S8 SEM cross-section image of VC12@Li.

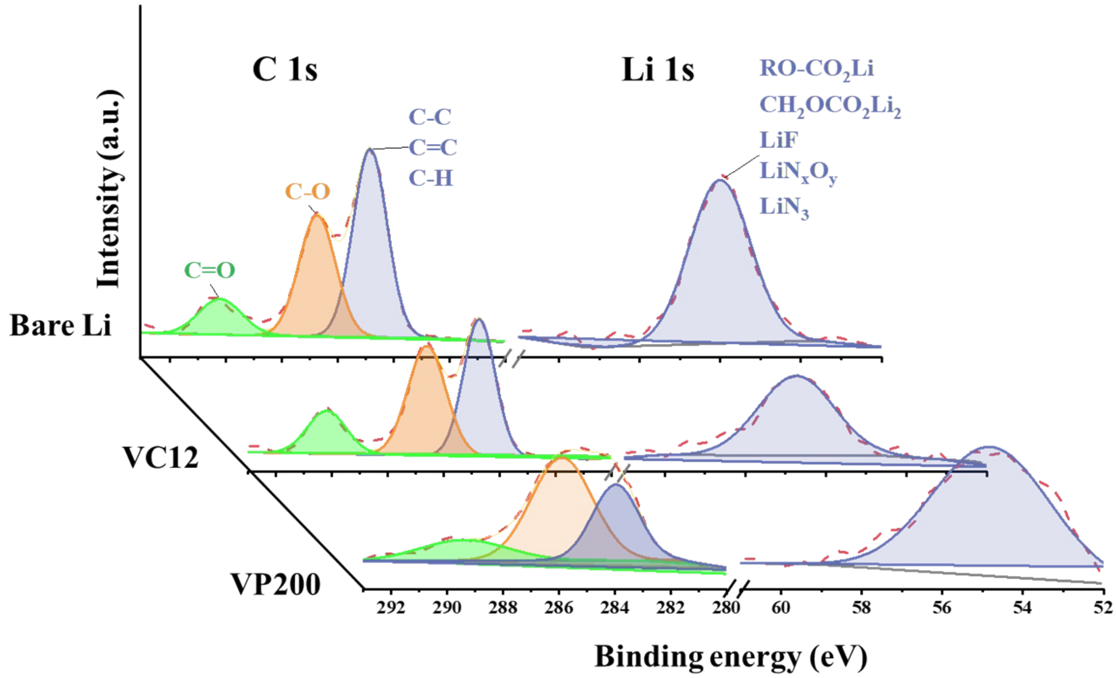


Fig. S9 XPS C 1s and Li 1s spectra of Bare Li, VC12@Li, and VP200@Li using 1 M $LiPF_6$ in EC/DEC (1:1, v/v). The Li|LFP, VC12@Li|LFP, and VP200@Li|LFP cells were disassembled after 100 cycles at 1C.

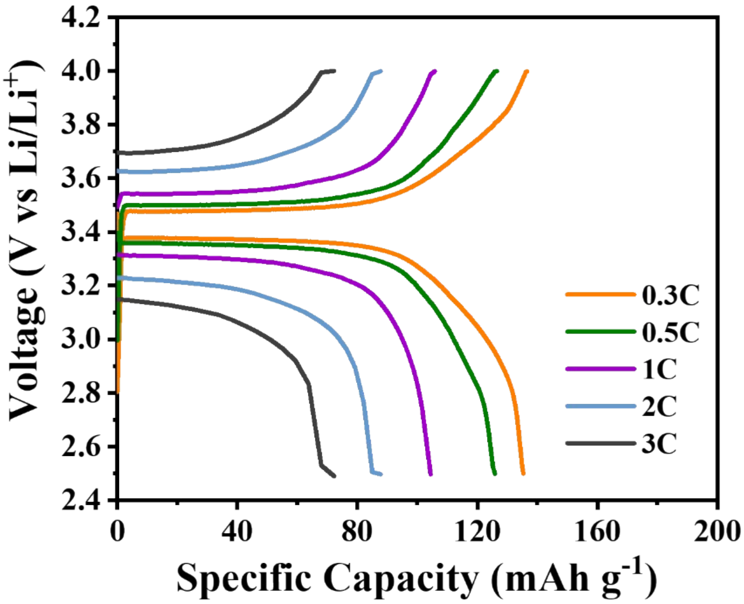


Fig. S10 Charge-discharge curves of Li|LFP in 1 M LiTFSI in DOL/DME (1:1, v/v) containing 2 wt% $LiNO_3$.

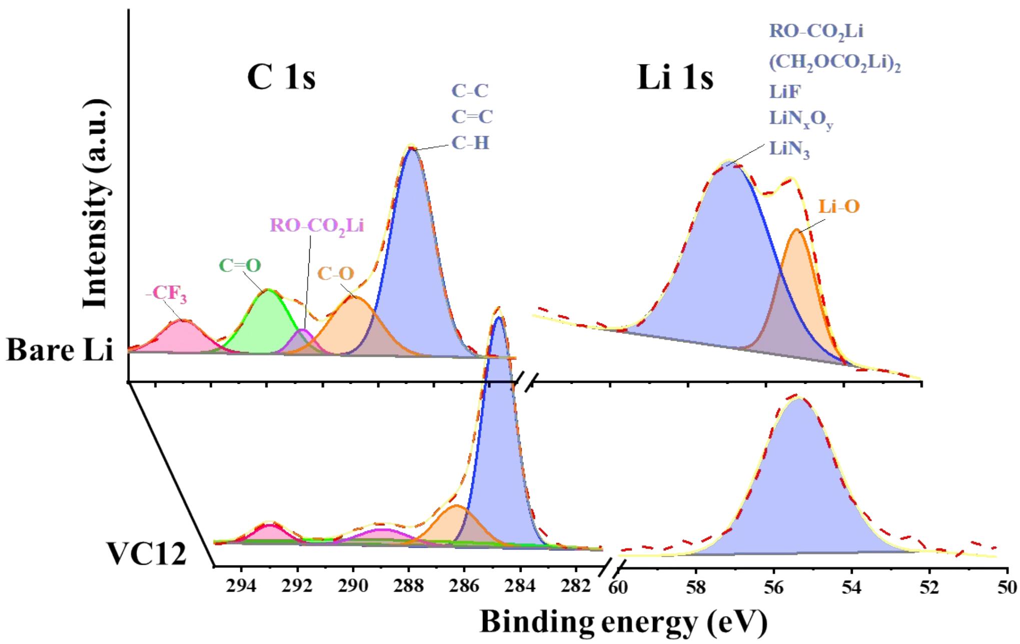


Fig. S11 XPS C 1s and Li 1s spectra of Bare Li, VC12@Li using 1 M LiTFSI in DOL/DME (1:1, v/v) containing 2 wt% $LiNO_3$. The Li|LFP and VC12@Li|LFP cells were disassembled after 100 cycles at 1C.

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