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

Long-cycling and Safe Lithium Metal Batteries enabled by the Synergetic Strategy of an Ex-situ Anodic Pretreatment and an In-built Gel Polymer Electrolyte

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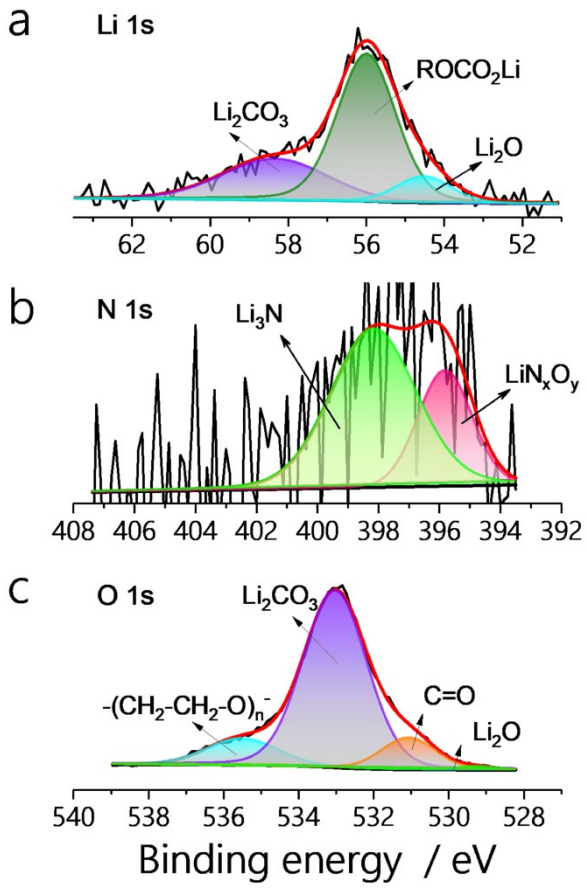

Figure S1. XPS analysis of Artificial SEI on Li metal after treated in 3 M $LiNO_3$-TEGDME for 12 h. (a) Li 1s spectra, (b) N 1s spectra, (c) O 1s spectra.

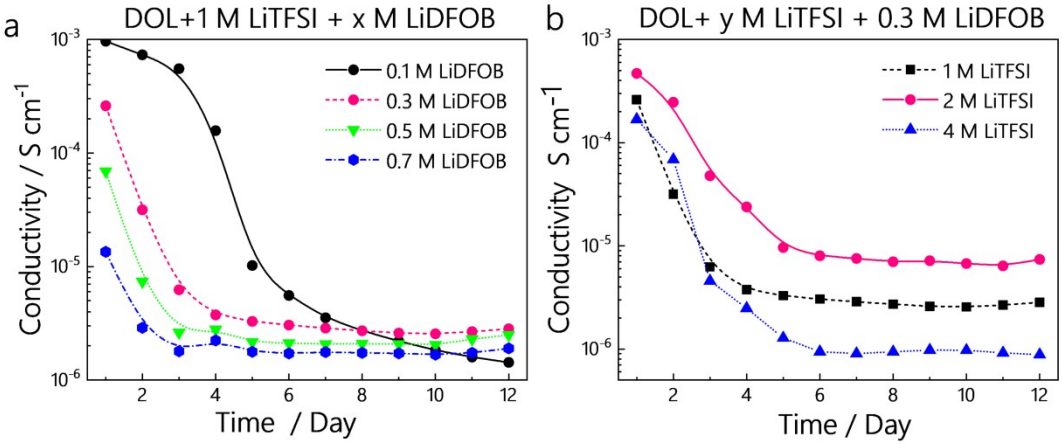

Figure S2. Ionic conductivity versus polymerization time for the GPEs with different concentrations of LiDFOB + 1 M LiTFSI (a) and variable concentrations of LiTFSI + 0.3 M LiDFOB (b) at room temperature.

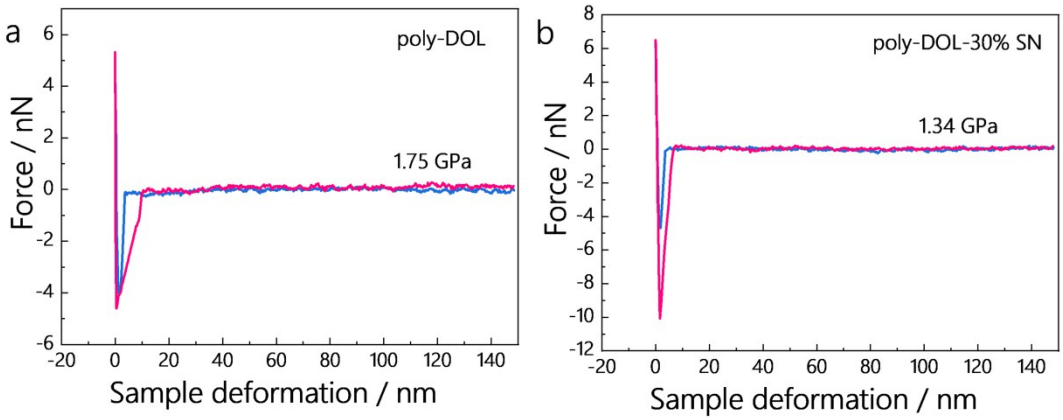

Figure S3. Force-displacement plots of poly-DOL-based GPEs with (a) 0 wt.% and (b) 30 wt.% SN.

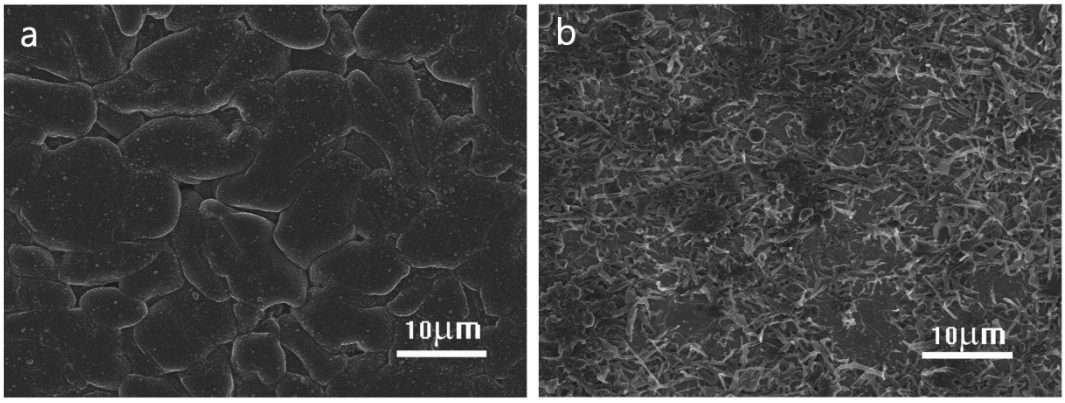

Figure S4. Top FE-SEM images of Li deposition obtained by plating 1 mAh cm^{-2} Li on Cu substrate at 0.1 mA cm^{-2} in (a) pretreated-Li|poly-DOL GPE|Cu and (b) untreated-Li|poly-DOL GPE|Cu cells.

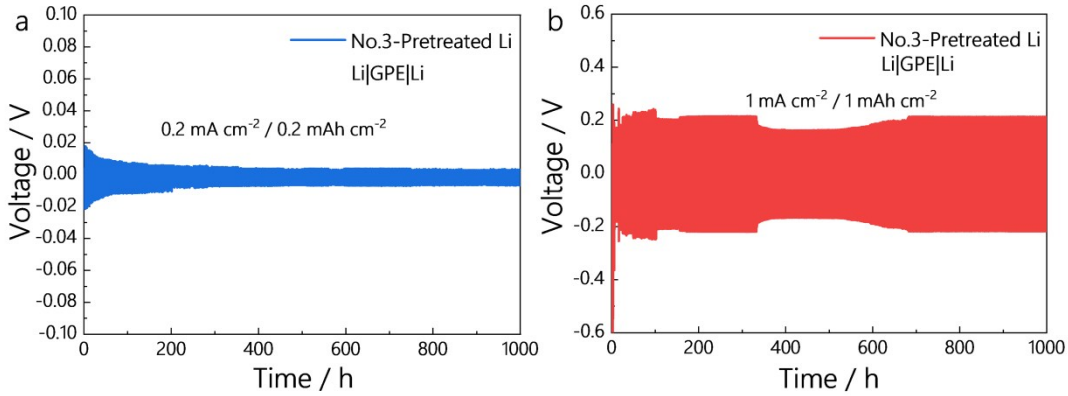

Figure S5. Galvanostatic cycling curves of Li|poly-DOL GPE|Li symmetric cells at (a) 0.2 mA cm^{-2} and (b) 1 mA cm^{-2} with a cut-off capacity of 0.2 mAh cm^{-2} and 1 mAh cm^{-2}, respectively.

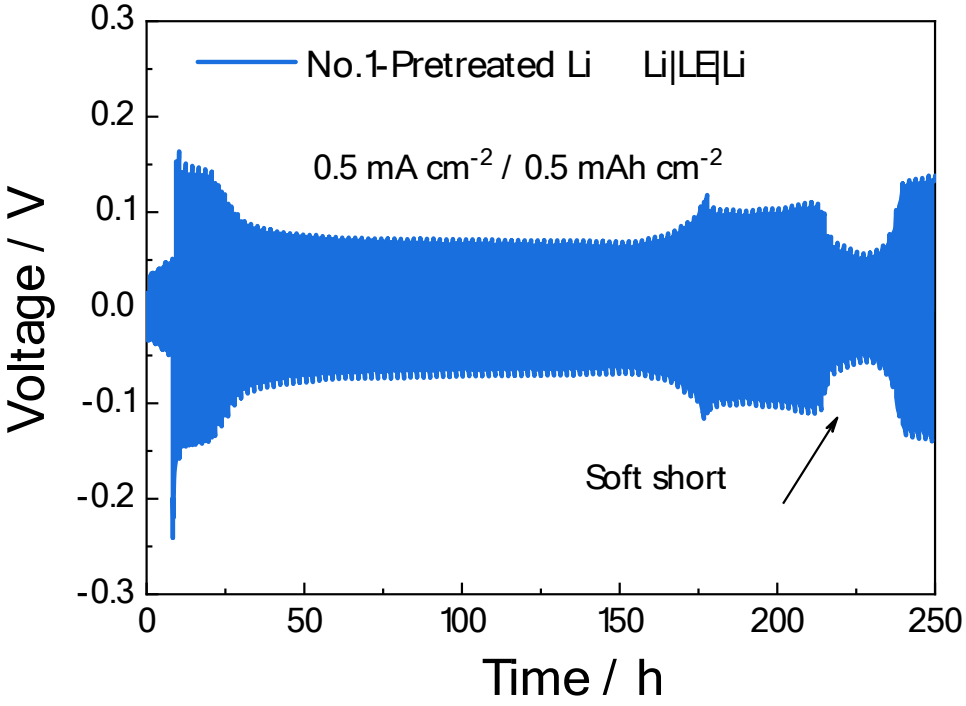

Figure S6. Galvanostatic cycling curves of Pretreated Li|LE| Li symmetric cells at 0.5 mA cm^{-2} with a cut-off capacity of 0.5 mAh cm^{-2}.

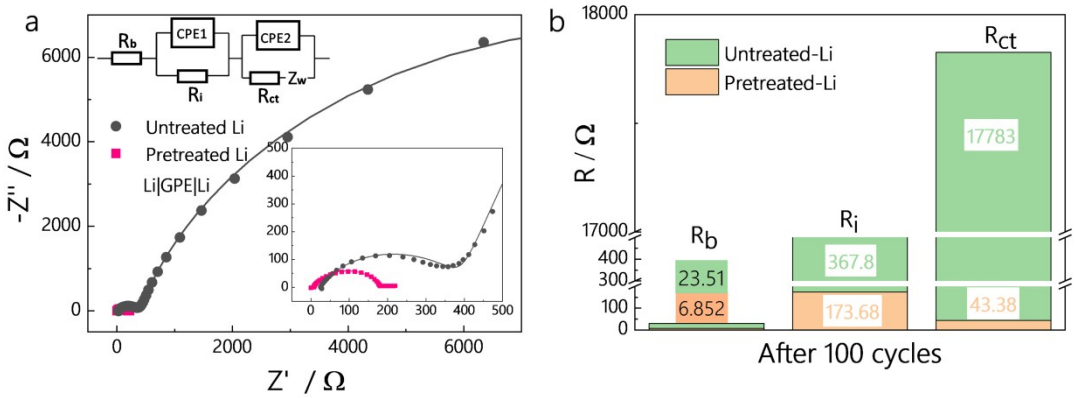

Figure S7 (a) EISs with enlarged view shown in the inset and (b) corresponding fitting results of Li|poly-DOL GPE|Li after 100 cycles at 0.5 mA cm^{-2}.

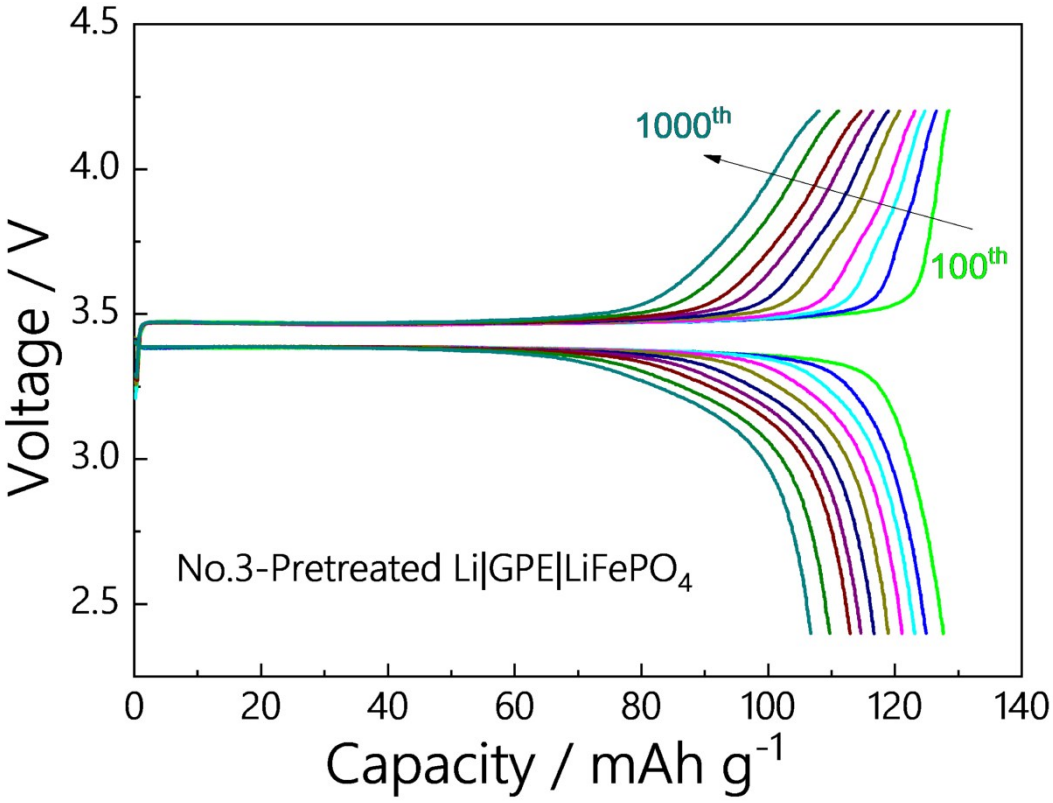

Figure S8. The charge-discharge curves of pretreated-Li|poly-DOL GPE|$LiFePO_4$ cell at 1 C after various cycles.

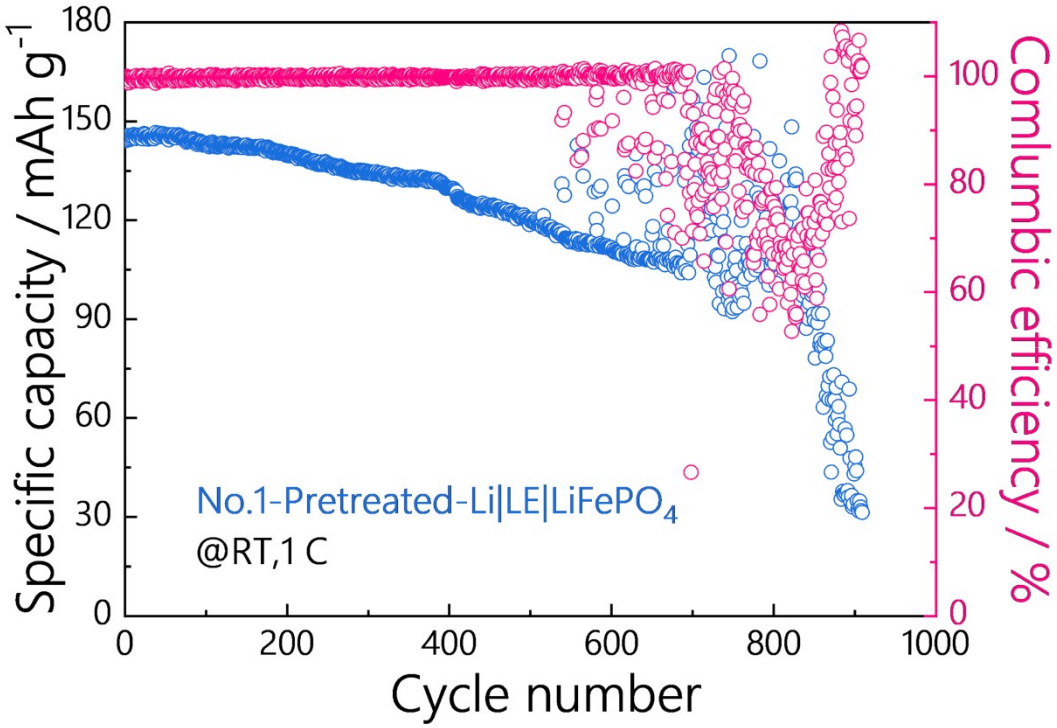

Figure S9. Cycling performance of pretreated-Li|LE|$LiFePO_4$ battery at 1 C.

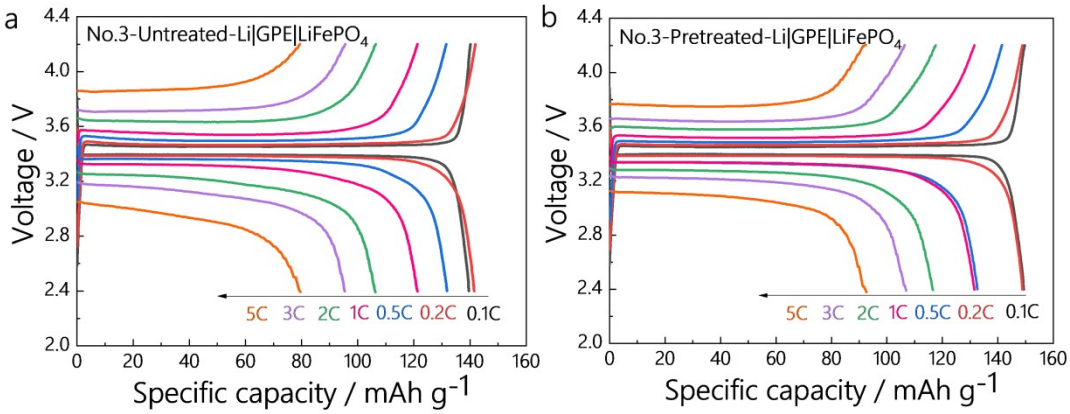

Figure S10. The charge-discharge curves of (a) untreated-Li|poly-DOL GPE|$LiFePO_4$ and (b) pretreated-Li|poly-DOL GPE|$LiFePO_4$ cells at various rates.

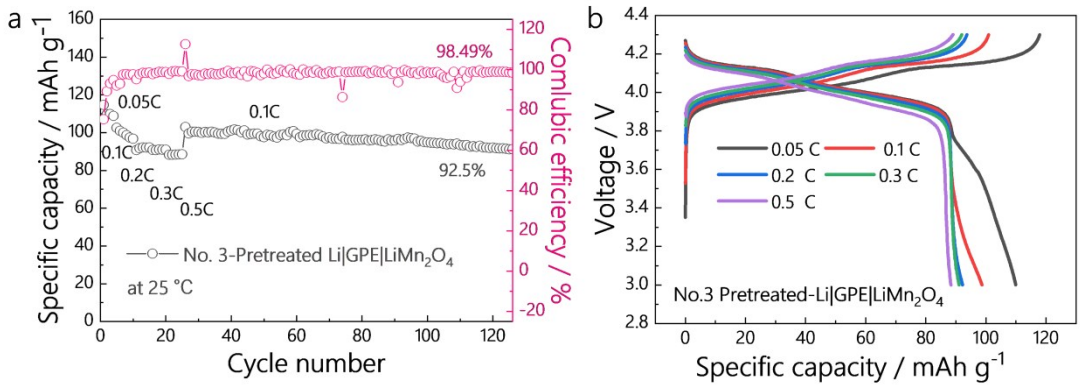

Figure S11. (a) Rate performances and (b) corresponding charge-discharge curves of pretreated-Li|GPE|$LiMn_2O_4$ battery under room temperature.

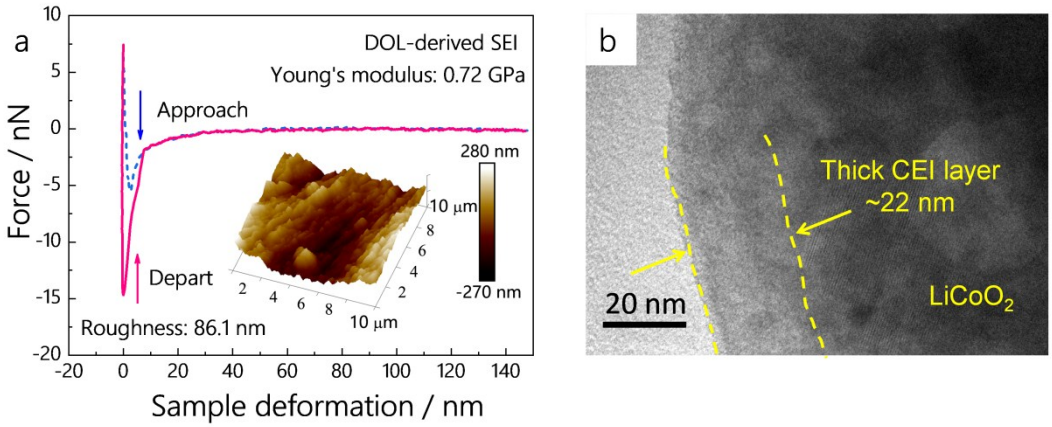

Figure S12. (a) Liquid DOL-strived SEI and the inset image is the corresponding 3D AFM scanning image of the SEI layer. (b) TEM image of the $LiCoO_2$ cathode surface recovered from pretreated-Li|LE|$LiCoO_2$ cell after 2 cycles at 40 °C.

Table S1. The cell performances of quasi-solid/solid state batteries based on GPE/SPE via in situ polymerization.

electrolyte	cathode	anode	Polymerization condition	Ionic conductivity	Anti-oxidation potential	Cell performance	Test condition	Ref.
PMMA+ EC/DEC	$LiNi_{0.5}Mn_{1.5}O_4$	Li	AIBN@50°C $LiPF_6$@RT	6.79×10^{-4} Scm^{-1} @RT	5.2V	131.7 mAh g^{-1} at first discharge, 78.9% capacity retention after 500 cycles	0.1C, 25°C	1
	$LiNi_{0.5}Mn_{1.5}O_4$	$Li_4Ti_5O_{12}$				128 $mAhg^{-1}$ at first discharge, 88.4% capacity retention after 100 cycles	0.1C, 25°C	
Poly-DOL+ DME	$LiFePO_4$	Li	$LiPF_6$@RT	3.8×10^{-3} Scm^{-1} @RT	4.6V	138 $mAhg^{-1}$ at first discharge, 95.6% capacity retention after 700 cycles	0.5C, RT	2
	NCM622	Li				164 $mAhg^{-1}$ at first discharge, 91.5% capacity retention after 100 cycles	0.1C, RT	
	S	Li				1005$mAhg^{-1}$ at first discharge, 73.7% capacity retention after 500 cycles	0.5C, RT	

Poly-DOL	$LiFePO_4$	Li	$Al(OTf)_3$@RT	1×10^{-3} Scm^{-1} @RT	> 5V	~93 $mAhg^{-1}$ at first discharge, 75% capacity retention after 700 cycles	1C, RT	3
	NCM622	Li				~170 $mAhg^{-1}$ at first discharge, 95% capacity retention after 5 cycles	1C, RT	
	S	Li				~1240 $mAhg^{-1}$ at first discharge, 42% capacity retention after 100 cycles	0.1C, RT	
PVCA	$LiCoO_2$	Li	AIBN, @60°C, 80°C	9.82×10^{-5} Scm^{-1} @50°C	4.5V @50°C	146 $mAhg^{-1}$ at first discharge, 84.2% capacity retention after 150 cycles	0.1C, 50°C	4
PFEC	$LiNi_{0.5}Mn_{1.5}O_4$	Li	$Sn(Oct)_2$ @80°C, 100°C	1.5×10^{-4} Scm^{-1} @25°C	>5.5V	~110.3 $mAhg^{-1}$ at first discharge, 83.4% capacity retention after 50 cycles	0.2C, RT	5
	$LiCoO_2$	Li				~162.3	0.1C, RT	

						mAhg^{-1} at first discharge, 92.4% capacity retention after 50 cycles		
PETEA+ DOL/DME	S	Li	AIBN@70°C	1.13×10^{-2} Scm^{-1} @25°C	4.73V	~646.8 mAhg^{-1}at first discharge, 81.9% capacity retention after 400 cycles	0.5C, 25°C	6
PETEA+ EC/DEC/EMC	NCA	graphite	AIBN@70°C	8.46×10^{-3} Scm^{-1} @25°C	>4.5V	~1.88 Ah at first discharge, 92.5% capacity retention after 200 cycles	5C, 25°C	7
	NCA	Si/C				~2.03 Ah at first discharge, 81.2% capacity retention after 200 cycles	5C, 25°C	
PTTE+ EC/DEC/DMC	LFP	Li/CF	$LiBF_4$@RT	9.6×10^{-4} Scm^{-1} @RT	>5V	146.6 mAhg^{-1} at first discharge, 88% capacity retention after 120 cycles	0.2C, RT	8
PVA-CN+ SN+PAN	LFP	Li	$LiPF_6$@70°C	4.49×10^{-4} Scm^{-1}	>5V	154.6 mAhg^{-1} at	0.1C, RT	9

				@25°C		first discharge, 96.7% capacity retention after 100 cycles		
TPGDA+SiO_2+ EC/EMC/DMC	LFP	Li	AIBN@60°C	1.74×10^{-3} Scm^{-1} @25°C	4.91V	159.3 $mAhg^{-1}$ at first discharge, 100.2% capacity retention after 200 cycles	0.2C, 25°C	10
C-PEGDE	LFP	Li	LiDFOB@80°C	8.9×10^{-5} Scm^{-1} @RT	4.5V	128 $mAhg^{-1}$ at first discharge, 74.2% capacity retention after 100 cycles	0.1C, RT	11
Poly-DOL+SN	LFP	Li	LiDFOB@60°C	3.9×10^{-4} Scm^{-1} @RT	>5V	126.5 $mAhg^{-1}$ at first discharge, 83.55% capacity retention after 1000 cycles	1C, RT	This work
	$LiMn_2O_4$	Li				101.0 $mAhg^{-1}$ at first discharge, 92.5% capacity retention after 100 cycles	0.1C,RT	
	$LiCoO_2$	Li				137.2 $mAhg^{-1}$ at	0.1C, 40℃	

						first discharge, 57.9% capacity retention after 60 cycles		

Reference

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