Supporting Information

Enabling Highly Stable Lithium Metal Battery by Dual-function Additive Catalyzed In-Built Quasi-Solid-State Polymer Electrolytes

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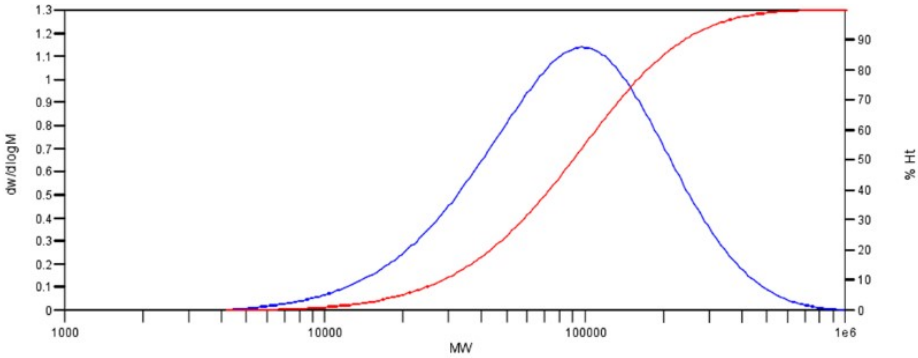

MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	99170	57061	114133	196017	296756	104281	2.00019

Figure S1. GPC data of Mg-PDOL-FEC with THF as the solvent.

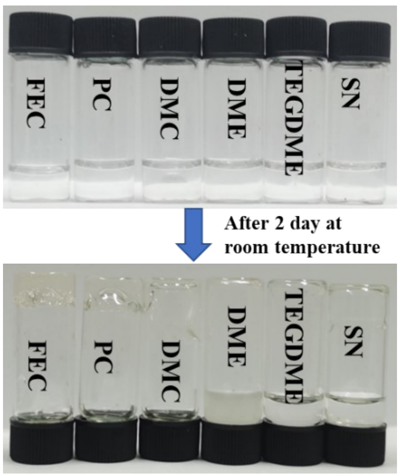

Figure S2. Photographs of Mg-PDOL-X electrolyte (1M LiTFSI in DOL:X (1:1=v:v) with 0.5 wt% $Mg(OTf)_2$) before and after in-situ polymerization (X=FEC, PC (propylene carbonate) and DMC (Dimethyl carbonate), DME (1,2-Dimethoxyethane), TEGDME (Tetraethyleneglycol dimethyl ether), SN (Succinonitrile)). We can clearly observe that the addition of DME, TEGDME, SN will prevent $Mg(OTf)_2$ to initiate the polymerization of DOL, while the introduction of FEC, propylene carbonate (PC), Dimethyl carbonate (DMC) and other ester plasticizers will facilitate the polymerization process of DOL.

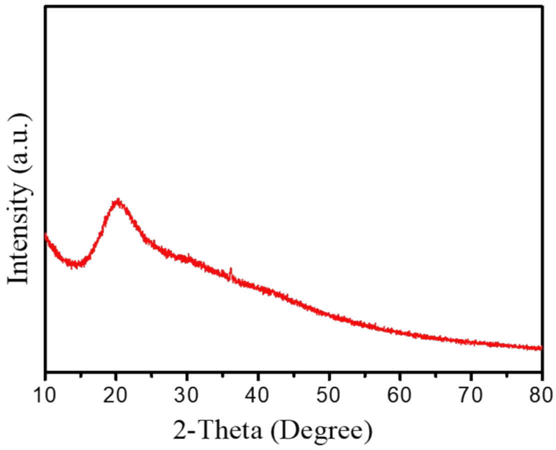

Figure S3. XRD of Mg-PDOL-FEC

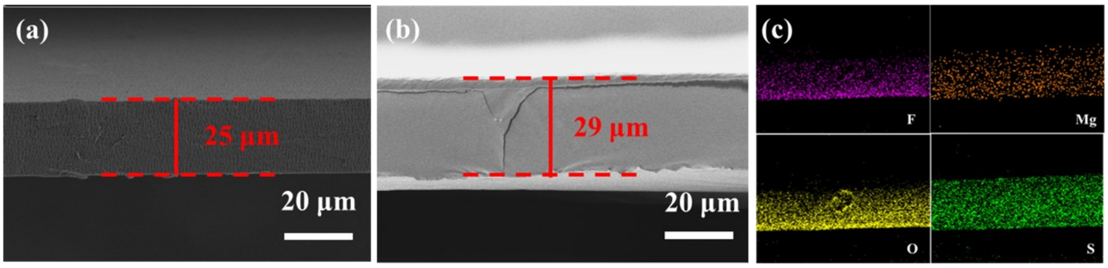

Figure S4. (a) SEM images of cross-section of the Celgard 3501 separator. (b) SEM images of cross-section of the Celgard 3501 separator after Mg-PDOL-FEC infiltration. (c) Energy Dispersive Spectroscopy (EDS) mapping images of cross section of the Mg-PDOL-FEC electrolyte after in-situ polymerization.

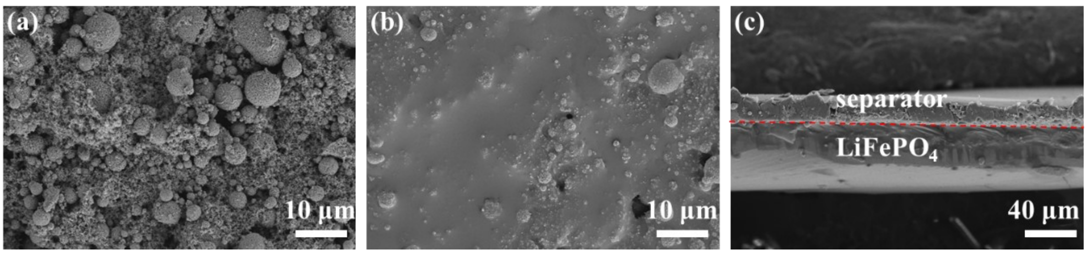

Figure S5. (a) SEM image of surface of pristine $LiFePO_4$ electrode; (b) SEM image of surface of $LiFePO_4$ electrode after in-situ polymerization (Mg-PDOL-FEC sample); (c) SEM images of cross section of $LiFePO_4$ electrode after in-situ polymerization (Mg-PDOL-FEC sample).

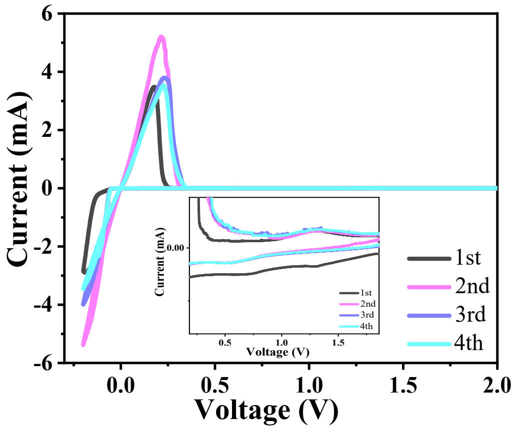

Figure S6. CV curves of the Li|DOL-FEC|SS cells.

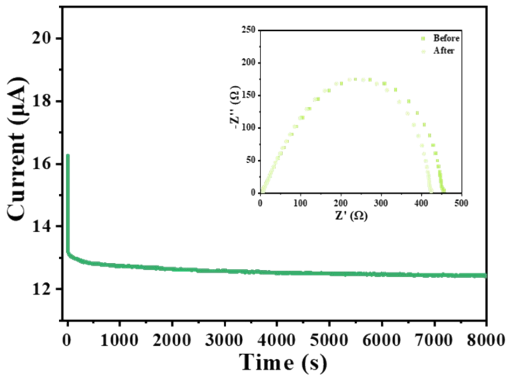

Figure S7. Chronoamperometry curves with a step voltage of 10 mV (The insets displayed EIS plot before and after polarization) of cells with Mg-PDOL electrolyte.

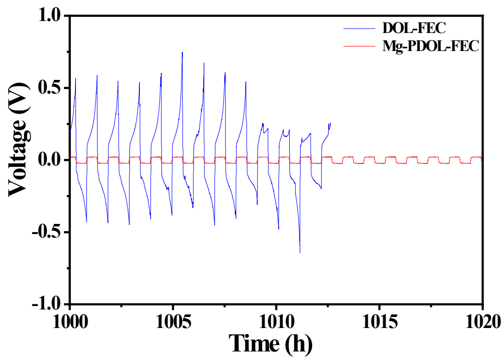

Figure S8. Corresponding enlarged voltage plots at 0.5 mA cm^{-2} and 0.25 mAh cm^{-2} from 1000 to 1020 h.

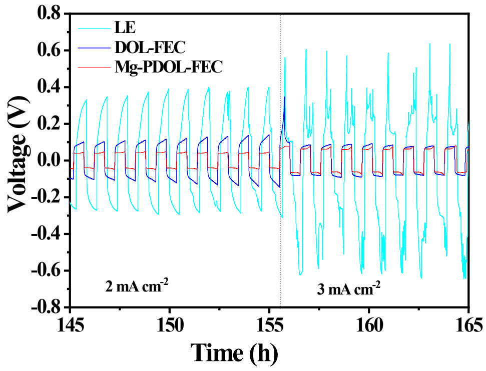

Figure S9. Corresponding enlarged voltage plots at different current densities from 145 to 165 h.

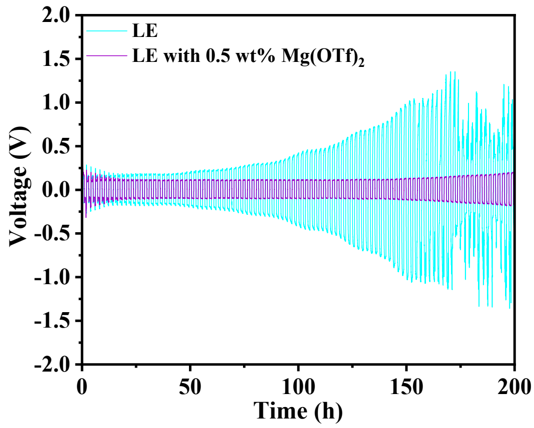

Figure S10. Voltage profiles of Li//Li symmetrical cells of LE and LE with 0.5wt% $Mg(OTf)_2$ electrolyte at 2 mA cm^{-2}, 2 mAh cm^{-2}.

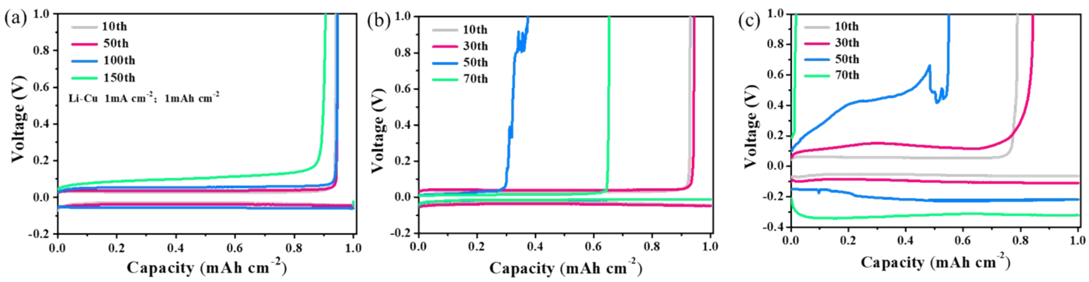

Figure S11. Plating/stripping profiles for the Li metal on a Cu foil substrate at 1 mA cm^{-2} in (a) Mg-PDOL-FEC, (b)DOL-FEC, and (c) LE;

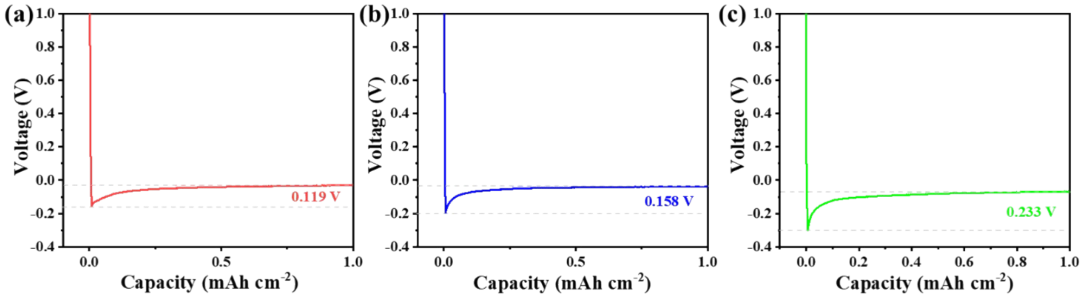

Figure S12. Voltage *vs* time curves of Li plating on Cu foil with Mg-PDOL-FEC, DOL-FEC, and LE electrolyte at 1 mA cm^{-2}. The overpotential of the Cu|Mg-PDOL-FEC|Li cell was only 0.119 V, much lower than that of Cu|DOL-FEC|Li cell (0.158 V) and Cu|LE|Li (0.233 V).

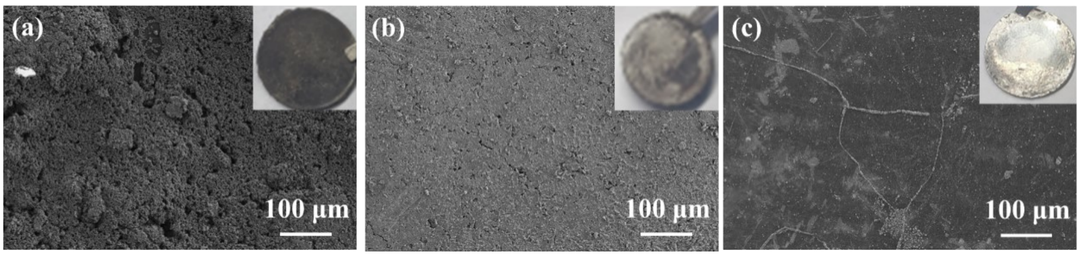

Figure S13. The surface SEM images of Li metal anodes, obtained from the Li//Li cells after 100 cycles, cycled in cells with a current density of 1 mA cm^{-2}, and 1mAh cm^{-2}. The inset is the digital picture. (a) LE battery. (b) DOL-FEC battery. (c) Mg-PDOL-FEC battery.

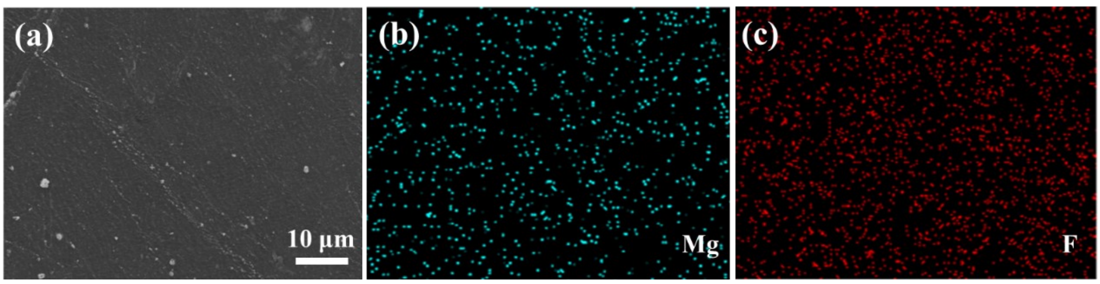

Figure S14. (a)The surface SEM images of Li metal anodes disassembled from the Li|Mg-PDOL-FEC|Li batterie after 100 cycles with a current density of 1 mA cm^{-2}, and 1mAh cm^{-2}. And corresponding EDS element mappings of (b) Mg, (c) F.

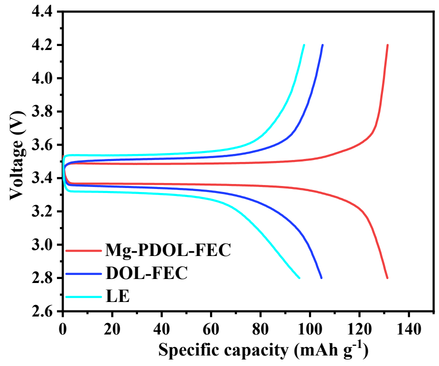

Figure S15. Discharge/charge voltage profiles of Li |Mg-PDOL-FEC|LFP full cells at 450th cycle.

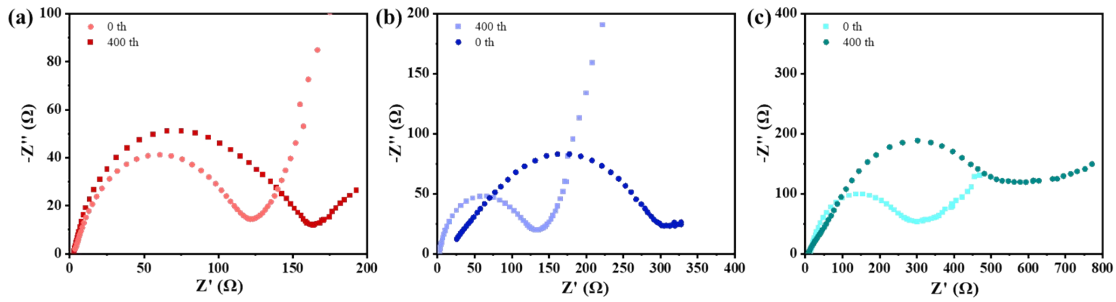

Figure S16. AC impedance spectra of Li //LFP cells. (a) Mg-PDOL-FEC; (b) DOL-FEC; (c)LE.

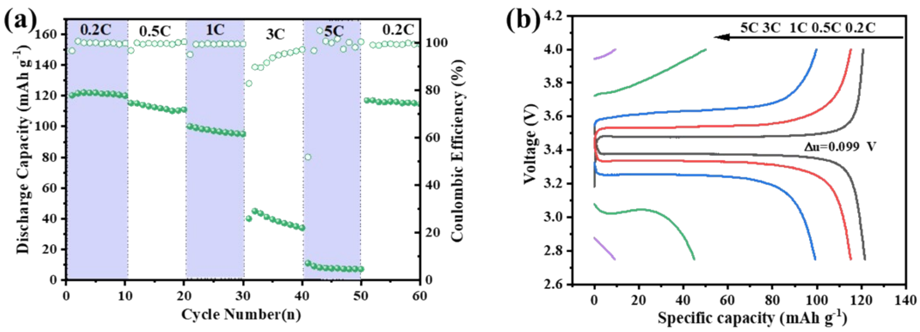

Figure S17. Rate performances and typical charge-discharge curves of Li /Mg-PDOL/LFP cells at room temperature.

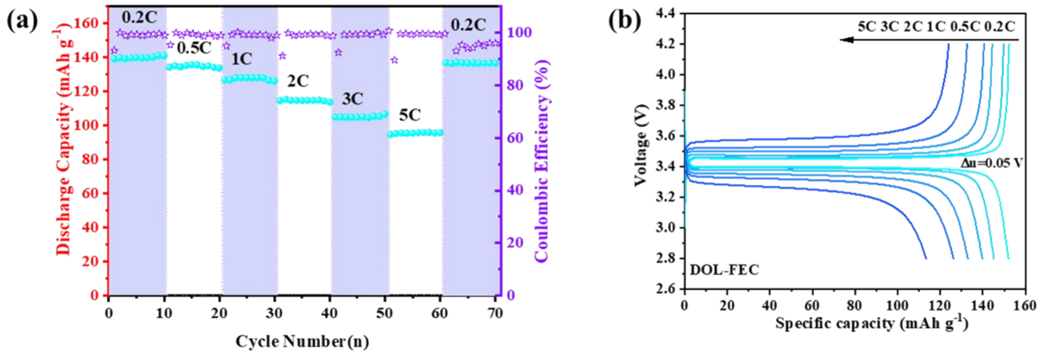

Figure S18. Rate performances and typical charge-discharge curves of Li /LE/LFP cells.

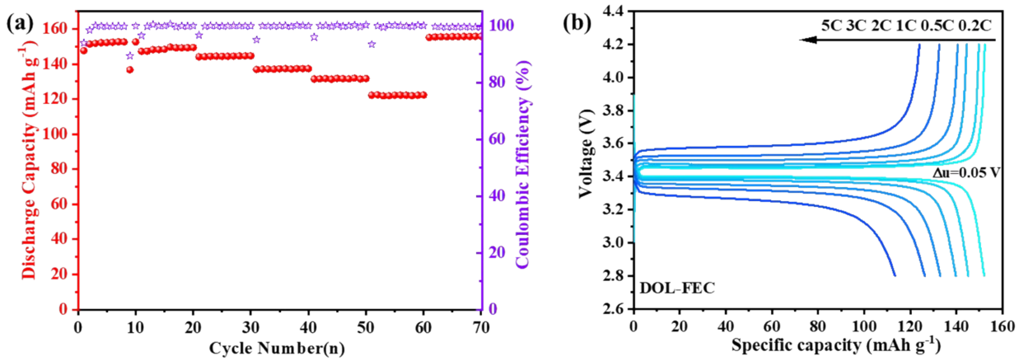

Figure S19. Rate performances and typical charge-discharge curves of Li/DOL-FEC/LFP cells.

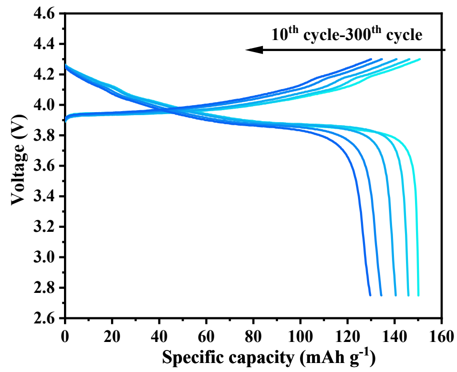

Figure S20. Typical charge-discharge curves of the Li/Mg-PDOL-FEC/ $LiCoO_2$-CIE cells at 0.5C at RT.

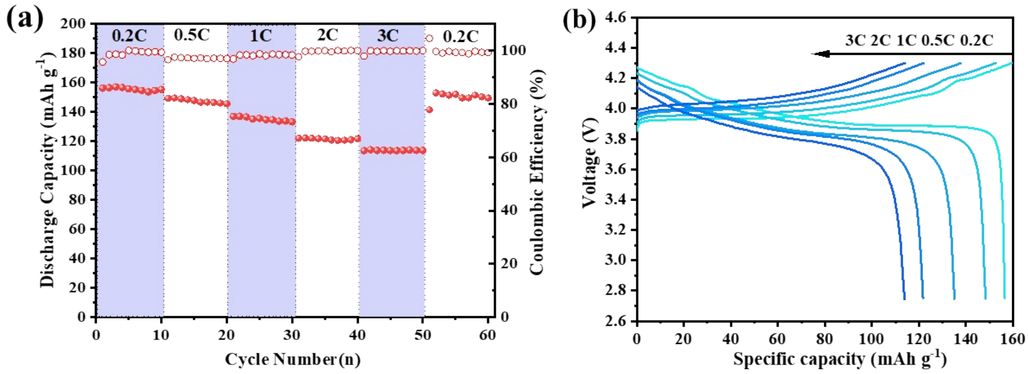

Figure S21. Rate performances and typical charge-discharge curves of Li/Mg-PDOL-FEC/ $LiCoO_2$-CIE cells.

Supplementary
Table S1. Polymerization degree of DOL in the electrolyte from monomer to polymer.

Sample	DOL (g)	1M LiTFSI (g)	$Mg(OTf)_2$	Plasticizer/ (g)	PDOL (g)	Polymerization conversion rate
Mg -PDOL-FEC	0.533	0.287	0.005	FEC/0.727	0.479	90%
Mg -PDOL-PC	0.533	0.287	0.005	PC/0.602	0.463	86%
Mg -PDOL-DMC	0.533	0.287	0.005	DMC/0.535	0.420	79%

The gel polymer is purified through the two-step method of acetone-dissolution and alcohol-precipitation to remove all the LiTFSI and $Mg(Otf)_2$, and the liquid phase containing plasticizer and unreacted DOL, and finally the PDOL is obtained. Therefore, the polymerization degree of DOL polymerized can be calculated according to the following equation.

$$Polymerization\ degree = \frac{m(PDOL)}{m(DOL)}$$

Table S2. Comparison of our work with previously reported polyether-based electrolytes via in-situ polymerization

Electrolytes (precursors +initiators)	Supporting skeleton	Li//Li cell performance (cycling life; highest current density; polarization voltage)	Li//Cu cell performance (average coulombic efficiency; current density)	Ionic transference number, conductivity	Battery performance	Reference
2M LiTFSI /DOL +300 ppm AlI_3 and 600 ppm LiDFOB	Glass fiber	>4000 h; 1.0 mA cm^{-2}, 1.0 mAh cm^{-2} at around 15 °C; <50 mV	99.08%; 0.1 mA cm^{-2}	t^+=0.62	$LiCoO_2$ (2~3 mg/cm^2)-CIE//Li, 45°C, 0.5 C, 700 cycles, capacity retention:89%	[1]
2M LiTFSI /DOL +3% TB	PP	>800 h; 1.0 mA cm^{-2}, 1.0 mAh cm^{-2}; <18 mV	98.1%; 0.5 mA cm^{-2}, 0.5 mAh cm^{-2};	t^+=0.58; 1.16 mS cm^{-1} (30°C)	Li// NCM622 (~4 mg/cm^2), 30°C, 0.5 C, 132 mAh g^{-1} after 200 cycles; 2C,122 mA h g^{-1} after 1200 cycles	[2]
1M LiTFSI /DOL +1% $LiPF_6$ and 1% PLAS	Commercial separator	500 h; 1mA cm^{-2}, 1mAh cm^{-2}; <50mV	/	0.2 mS cm^{-1} (30°C)	$LiFePO_4$ (3mg/cm^2)//Li, 30°C, 3 C, after 400 cycles, capacity retention :80%, capacity decay rate: 0.05%;	[3]
2M LiTFSI/ DOL and 30wt% SN+0.3M LiDFOB	Glass fiber	>1000 h; 1 mA cm^{-2}, 1 mAh cm^{-2}; <0.25 V	97.9%; 0.1 mA cm^{-2}, 0.1mAh cm^{-2};	0.39 mS cm^{-1} (RT)	$LiFePO_4$ (~2 mg/cm^2)//Li, RT, 1 C, 1000 cycles, capacity retention: 83.55%	[4]
2M LiTFSI/ DOL +10 mM	PDA/PVDF-HFP nonwoven	>250 h; 0.5 mA cm^{-2}, 1 mAh	/	t^+=0.59; 0.29 mS cm^{-1} (25°C)	$LiFePO_4$ (2.2 mg/cm^2)//Li, 20°C, 2 C, 800 cycles, capacity	[5]

$Al(OTf)_3$		cm^{-2}; <25 mV			retention: 82.5%; 0.2 C, after 200 cycles, 145.4 mA h/g, capacity decay rate: 94.8%	
1M LiTFSI/ DOL and 50wt% DME+4% acid-treated Al_2O_3	Celgard film	>1000 h; 1 mA cm^{-2}, 1 mAh cm^{-2}; <44 mV	/	t^+=0.74;3.37 $\times10^{-3}$ S cm^{-1}(RT)	$LiFePO_4$ (5 mg/cm^2)//Li,RT, 100 mA g^{-1}, from ~140 mAh g^{-1} to ~115 mAh/g after 200 cycles	[6]
2M LiTFSI/ DOL +0.3 M AlF_3 and 0.2 mM $Al(OTf)_3$	Celgard 3501	/	/	mS cm^{-1} level (RT)	NCM622//Li (3mAh/cm^2), RT, 0.5 C,30 cycles, capacity retention:＞80%	[7]
1M LiTFSI/ DOL and 50wt% MP + $LiPF_6$	Celgard 2500	>2000 h; 0.1 mA cm^{-2}, 0.1mAh cm^{-2};	94%; 0.1 mA cm^{-2}, 0.2mAh cm^{-2};	t^+=0.61;1.0 mS cm^{-1} (−30 °C)	$LiFePO_4$ (~2mg/cm^2)//Li, 23℃, 1 C, 134 mAh g^{-1} after 2000 cycles, capacity retention: 89%	[8]
2M LiTFSI/ DOL +0.5 mM $Al(OTf)_3$	Celgard 3501	>200 h; 1 mA cm^{-2}, 1 mAh cm^{-2};	~98%; 1 mA cm^{-2}, 1 mAh cm^{-2};	>1 mS cm^{-1}	S (2mg/cm^2)//Li, RT, 0.1C, 100 cycles, capacity retention: 89%; $LiFePO_4$ (5mg/cm^2)//Li,23℃, 1 C, no more than 100 mA h g-1 after 700 cycles	[9]
1M LiTFSI/ DOL And 20wt%	glass fiber	>900 h; 0.5 mA cm^{-2}, 0.5 mAh cm^{-2}; <45 mV;	/	t^+=0.62; 0.24mS cm^{-1} (30 °C)	$LiFePO_4$ (~2mg/cm^2)//Li, 30 ℃, 1C, from 135.6 mAh g^{-1} to 105.7 mAh/g after 1000	[10]

TOCS+ 1M LiDFOB					cycles	
1M LiTFSI/ DOL and 50wt% DME+2M $LiPF_6$		>800 h; 0.5 mA cm^{-2}, 1 mAh cm^{-2}; <25 mV; >400 h; 1 mA cm^{-2}, 1 mAh cm^{-2};	~95%; 1 mA cm^{-2};	3.8 mS cm^{-1} (RT)	S (1.5 mg/cm^2)//Li, RT,0.5C, 741 mAh g^{-1} after 500 cycles, capacity retention: 73.7%; $LiFePO_4$ (5mg/cm^2)/// Li, RT, 0.5C, 700cycles, capacity retention: 95.6%;	[11]
1M LiTFSI/DOL and 50wt% FEC +0.5% $Mg(OTf)_2$	Celgard 3501	>1600 h; 0.5 mA cm^{-2}, 0.25mAh cm^{-2}; <45 mV; >400 h; 1 mA cm^{-2}, 0.5 mAh cm^{-2}; <55 mV;	94.3%; 1 mA cm^{-2}, 1 mAh cm^{-2};	t^+=0.61; 0.5 mS cm^{-1} (RT)	LFP (2.8~3 mg/cm^2)//Li, RT,1C, 2000 cycles, capacity retention: 94%; 2C, 800 cycles, capacity retention: 87%; $LiCoO_2$ (3~4 mg/cm^2)-CIE//Li, RT, 0.5 C, 300 cycles, capacity retention: 87%	**This work**

Reference

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