

# **Effects of Concentrated Salt and Resting Protocol on Solid Electrolyte Interface Formation for Improved Cycle Stability of Anode Free Lithium Metal Batteries**

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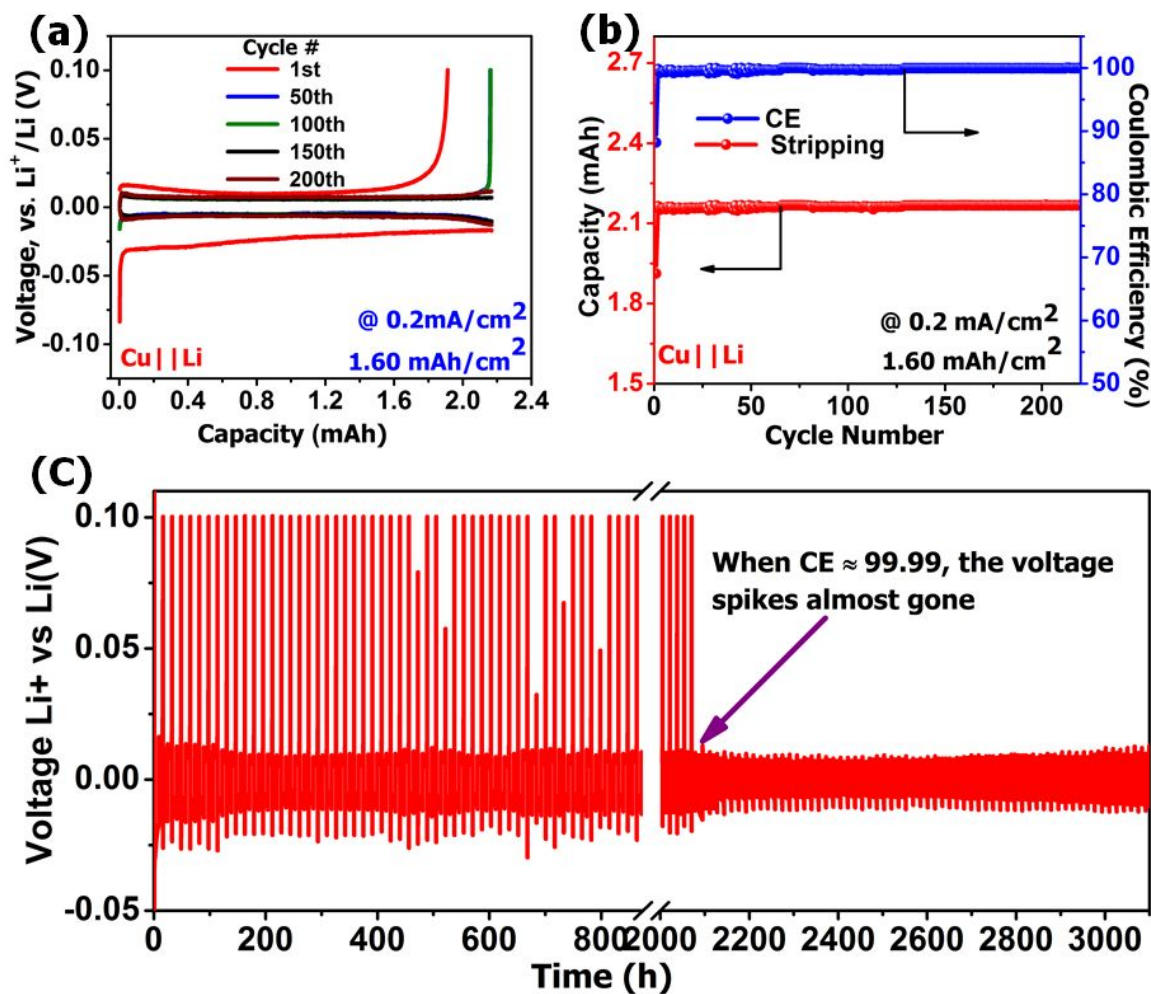
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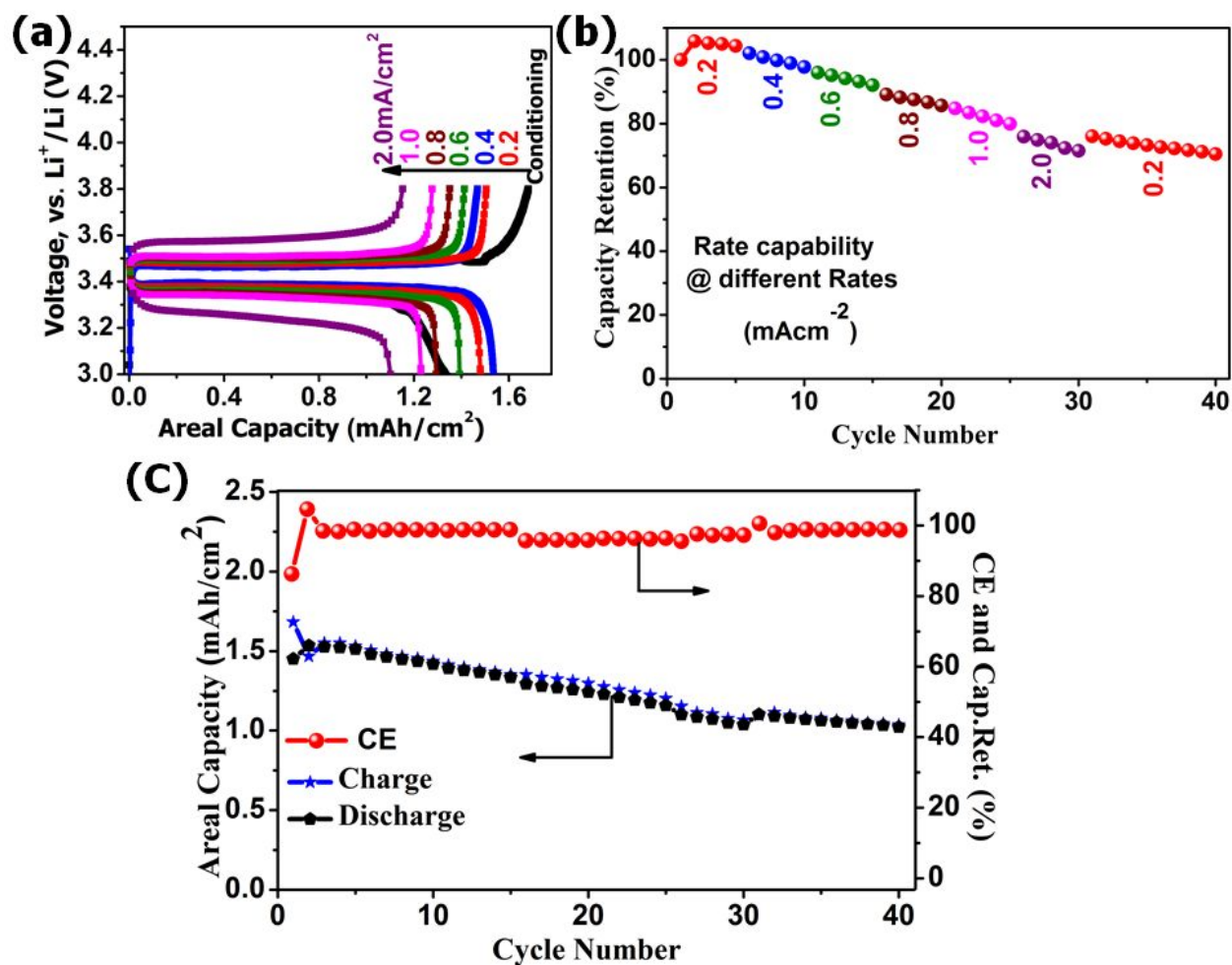
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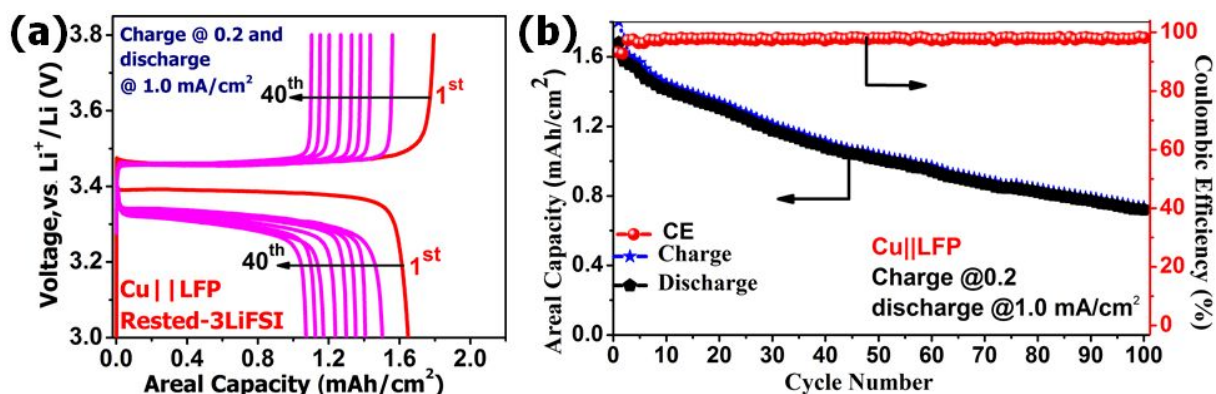
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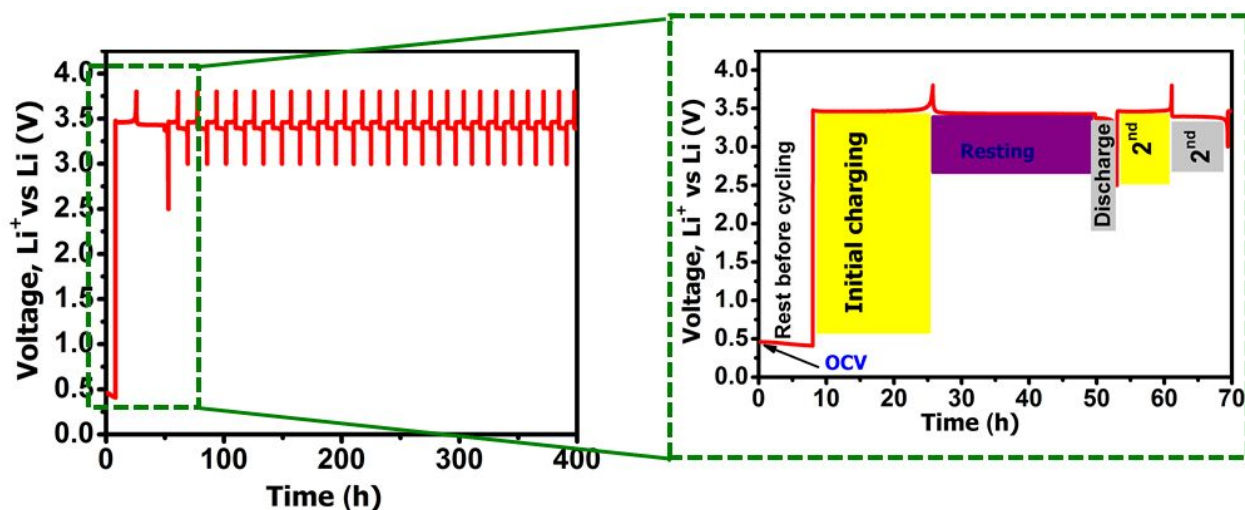
**Figure S1** Cycling performance of Cu || Li half-cell cycled at a rate of  $0.2 \text{ mA/cm}^2$  using the 3LiFSI electrolytes. A capacity of  $1.6 \text{ mAh/cm}^2$  was used to plate the Li metal, in which plating was controlled by time (for 8 hours) while stripping was voltage controlled at 0.1V. (a) Charge/discharge voltage profile, (b) Coulombic efficiency and stripping capacity (c) voltage-time graph for the first 1000 hours.



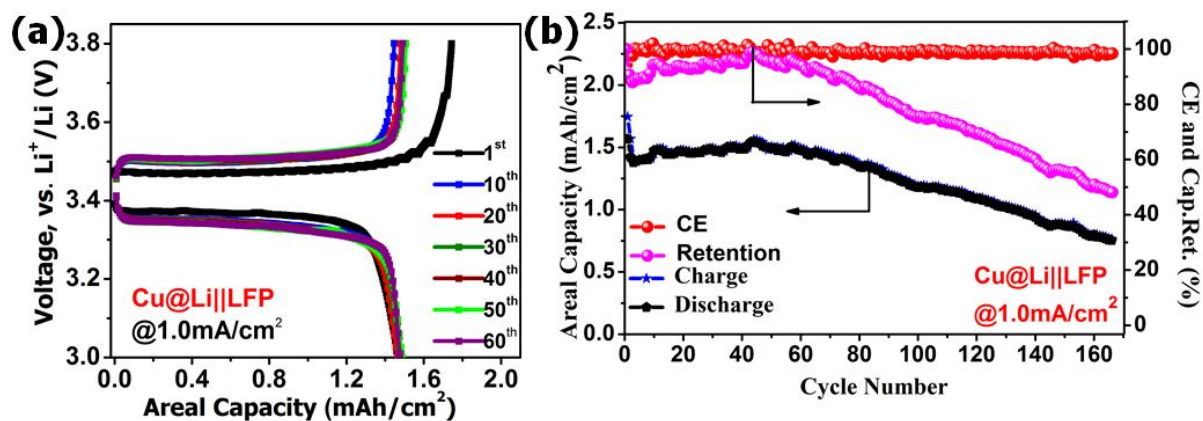
**Figure S2.** Rate capability of Cu||LFP cell cycled in 3LiFSI (ether-based electrolyte) preconditioning using the resting protocol. (a) charge-discharge voltage profile at different current densities as indicated by the color schemes (b) Discharge capacity retentions at different current densities and (c) Summarized cell performance of cell in 'a' that shows the extent of changing of each quantity with a change in applied current.



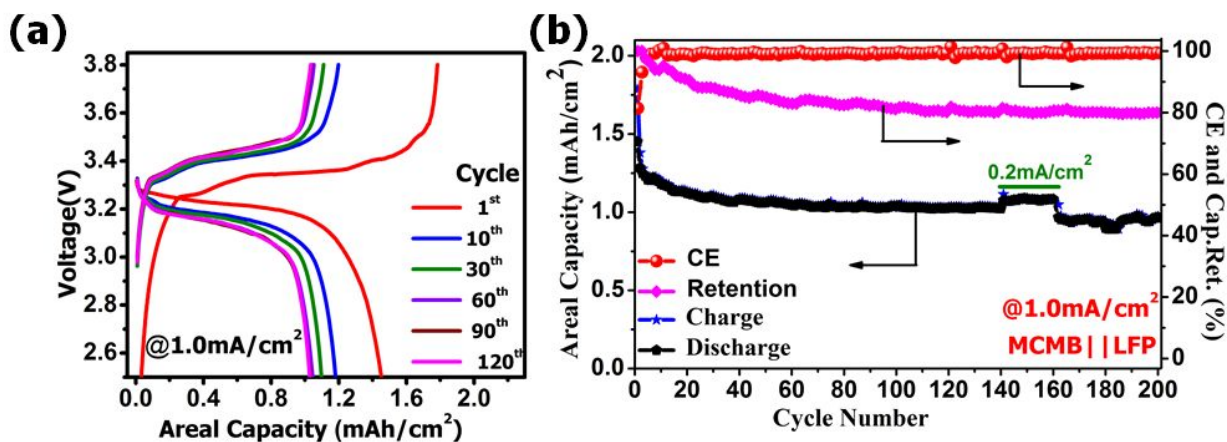
**Figure S3.** Electrochemical performance of Cu||LFP cell cycled in the laboratory-prepared 3LiFSI electrolyte initially conditioned using our cycling protocol in which the charging (0.2  $\text{mA}/\text{cm}^2$ ) and discharging (1.0  $\text{mA}/\text{cm}^2$ ) rates are varied after the initial conditioning process. (a) Charge-discharge voltage profile of the cell during the first 40 cycles (b) Summary of the performances like capacity, CE and capacity retention of the first 100 cycles.



**Figure S4.** Voltage-time graph of anode free battery cycled in 3LiFSI electrolyte using the optimized protocol @ 0.2  $\text{mA}/\text{cm}^2$ . The region showing the initial conditioning is enlarged and shown separately on the right-hand side of the figure for better clarity. Low OCV of the battery which is the typical property of the anode free battery is also pointed by an arrow.



**Figure S5.** Cu@Li||LFP full cell cycled in the 3LiFSI (ether-based electrolyte) using the optimized protocol at 1.0 mA/cm<sup>2</sup>. (a) Charge-discharge voltage profile. The less polarized curves drawn in black indicates the initial conditioning step as stated in the charge-discharge procedure. (b) Capacity and coulombic efficiency of the cell.



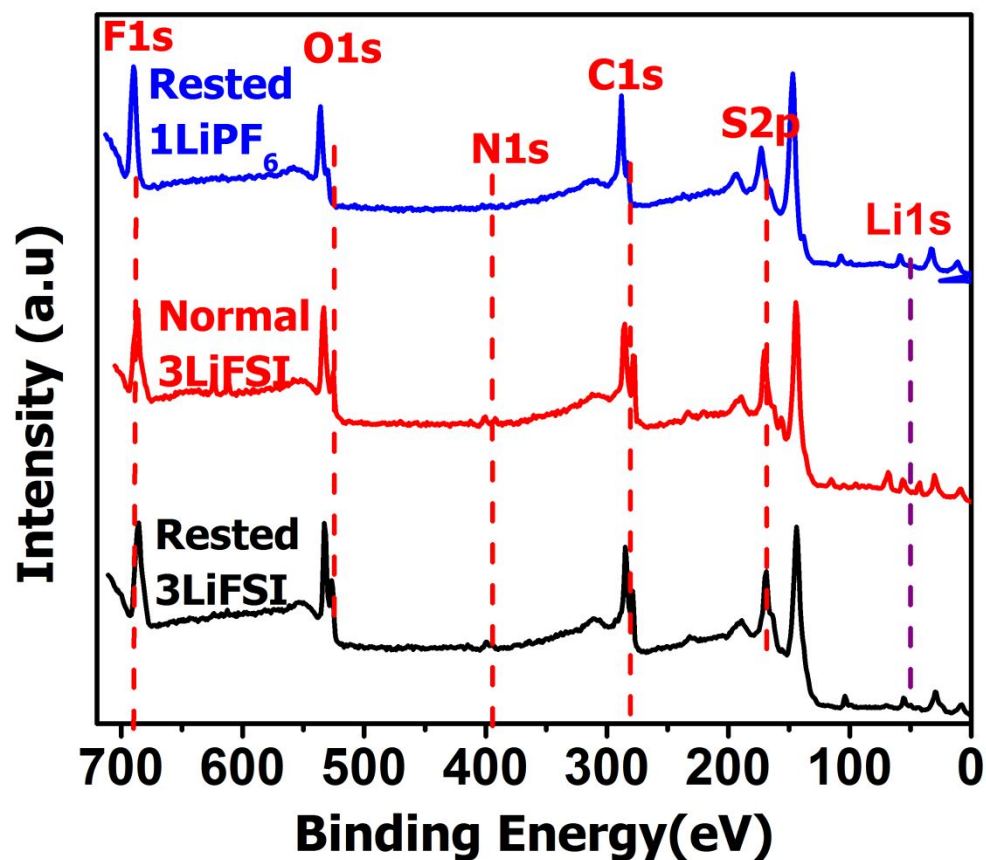
**Figure S6.** MCMB||LFP full cell cycled in the 3LiFSI (ether-based electrolyte) using the resting protocol at 1.0 mA/cm<sup>2</sup>. (a) Charge-discharge voltage profile. The less polarized curves drawn in red indicates the initial conditioning step as stated in the charge-discharge procedure. (b) Capacity and coulombic efficiency of the cell. The capacity increase between cycle 140-160 is

caused by decreasing the current density in which the capacity of the battery was increased by about 5%.

**Table S1.** Comparative summary of the real impedance of batteries at different discharge cycles.

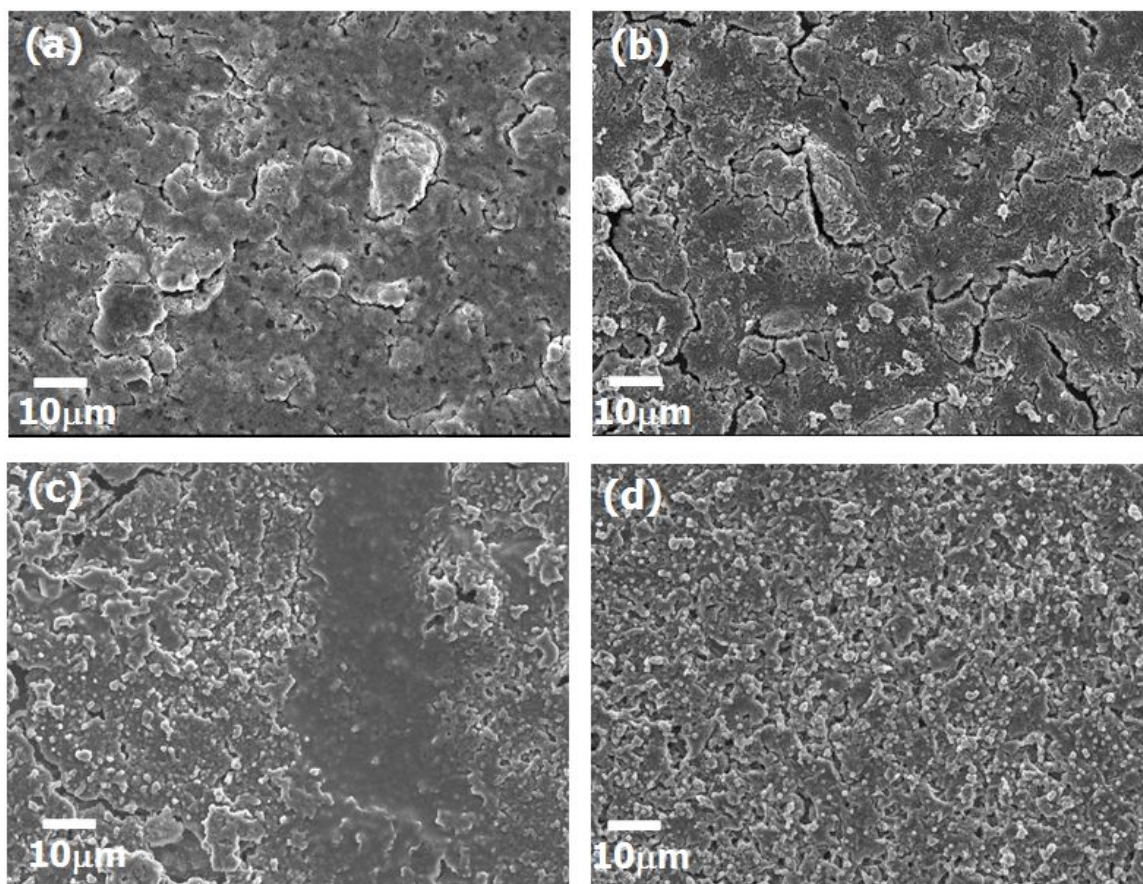
The data were obtained from Z-fit of Nyquist plot by EC-Lab software from **Figure 6**

Cycle Number	Electrolyte/Cycling strategy	Re (Z)/Ohm/Z-fit result	
		$R_s$	$R_{ct}$
1	Rested-1LiPF <sub>6</sub>	$2.93 \pm 0.42$	$32.34 \pm 0.62$
	Normal-3LiFSI	$4.24 \pm 0.38$	$19.28 \pm 0.45$
	Rested-3LiFSI	$6.63 \pm 0.38$	$18.63 \pm 0.43$
5	Rested-1LiPF <sub>6</sub>	$3.37 \pm 0.41$	$18.32 \pm 0.67$
	Normal-3LiFSI	$3.44 \pm 0.08$	$13.32 \pm 0.54$
	Rested-3LiFSI	$4.07 \pm 0.38$	$16.70 \pm 0.42$
10	Rested-1LiPF <sub>6</sub>	$3.37 \pm 0.41$	$23.64 \pm 0.62$
	Normal-3LiFSI	$3.81 \pm 0.10$	$13.14 \pm 0.63$
	Rested-3LiFSI	$5.51 \pm 0.41$	$17.68 \pm 0.75$
15	Rested-1LiPF <sub>6</sub>	$3.96 \pm 0.40$	$26.79 \pm 0.59$
	Normal-3LiFSI	$3.59 \pm 0.37$	$15.59 \pm 0.61$
	Rested-3LiFSI	$5.83 \pm 0.42$	$18.47 \pm 0.48$



**Figure S7.** XPS survey test showing the existence of all elements involved in the investigation from the surface analysis of the in-situ formed SEI. The electrolyte involved and the protocol indicated by the color scheme as it is written.





**Figure S8.** SEM morphological evaluation of Li-anode on Cu substrate retrieved from Cu || LFP cell after being cycled @ different rates using the resting protocol in the 3LiFSI electrolyte (a-b) Fully discharged state after cycled @ 0.5 mA/cm<sup>2</sup> (a) after 5 cycles (b) after 100 cycles (c-d) Fully discharged state after cycled @ 1.0 mA/cm<sup>2</sup> (c) after 5 cycles, (d) after 100 cycles.

## Supportive Note 1

Symmetrical cell configuration was used for the conductivity measurement, where a separator (Celgard 2325, 25 μm thick) soaked with a fixed amount of electrolyte which was sandwiched between two stainless steel as blocking electrodes. The EIS was measured at frequencies range  $f_i = 100$  kHz to  $f_f = 10$  mHz with a perturbation amplitude of  $\pm 10$  mV using a BioLogic Science



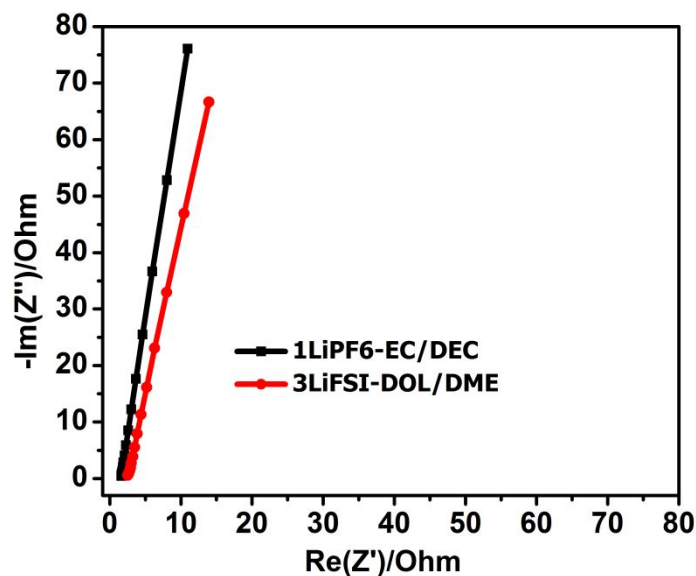
Instruments coupled with a Frequency Response Analyzer at 25°C. The reproducibility of impedance spectroscopy results was checked by the multiple experiments performed at room temperature. All results obtained for samples of the same composition did not differ by more than 5%. 3M LiFSI-DOL/DME, and 1M LiPF<sub>6</sub>-EC/DEC electrolytes were tested and the conductivity was calculated based on the equation (\*), where  $\sigma$  = electrolyte conductivity,  $l$  = distance between the electrode,  $R$ = solution resistance and  $A$  = area of the electrode.

$$\sigma = \frac{l}{RA} \quad (*)$$

Area of the stainless steel used for the EIS measurement was 2.011 cm<sup>2</sup> while the distance between the two electrodes is 2.5x10<sup>-3</sup> cm. Based on these numerical data and by the help of **Equation \***, the ionic conductivities of the three electrolytes were calculated and tabulated into Table S2

**Table S2:** Summary of the bulk resistances and ionic conductivity of electrolyte obtained from EIS measurement of Cu||Cu cell at 25 °C. The numerical values are obtained from EIS data in **Figure S9**.

Electrolyte	3M LiFSI-DOL/DME	1M LiPF <sub>6</sub> -EC/DEC
Bulk Resistance ( $\Omega$ )	0.337	0.185
Conductivity ( mS/cm)	3.68	6.72

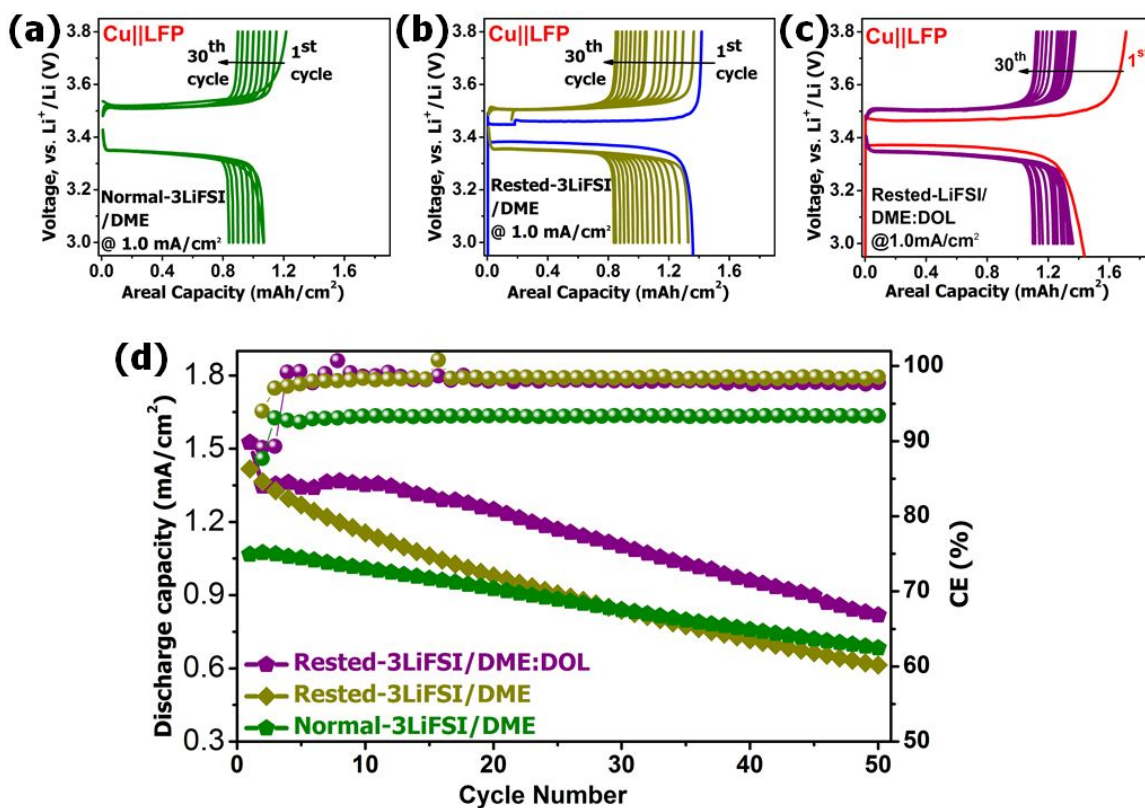


**Figure S9.** EIS measurements of as prepared symmetrical cell using disks of bare Cu on both side in a coin type cell. The EIS was measured at frequencies range  $f_1 = 100$  kHz to  $f_f = 100$  mHz with a perturbation amplitude of  $\pm 10$  mV using a BioLogic Science Instruments coupled with a Frequency Response Analyzer.

## Supportive Note 2

The electrochemical performances Cu||LFP cell cycled at  $1.0 \text{ mA/cm}^2$  in different electrolytes is given in Figure S10. Among all, the cyclic performance of the cell assigned as Normal-3LiFSI/DME is the worst. The discharge capacity and CE of this battery is relatively very poor. The battery showed very large voltage polarization than the rest (Figure S10a, d). On the other hand, the battery assigned as Rested-3LiFSI/DME showed an average performance relative to the rest two. The initial discharge capacity and CE of this cell was highly improved relative to the

Normal-3LiFSI/DME. However, the capacity retention of this cell is much poorer than the Rested-3LiFSI/DME: DOL. Thus based on Figure S7, Figure S10, and the existing literature, we can confirm that the presence of the DOL solvent in the 3M LiFSI electrolyte improves cyclic performance of the anode free batteries.



**Figure S10.** Electrochemical performance of anode free, Cu||LFP, cells in different electrolytes cycled at  $1.0 \text{ mA}/\text{cm}^2$  using different cycling protocols (a-c) Charge-discharge voltage profile of anode free cell assigned as (a) Normal-3LiFSI/DME, (b) Rested-3LiFSI/DME (C) Rested-3LiFSI/DME: DOL and (d) Comparison of discharge capacity and CE profiles of cells in 'a', 'b', & 'c'