Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Novel Cyclopentyl Methyl Ether Electrolyte Solvent with Unique Solvation Structure for Subzero (-40°C) Lithium-ion Battery

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Experimental Procedures:

Materials: The entire electrochemical test was carried out using half-cell configuration with Mesocarbon Microbeads Anode (MCMB) and Lithium metal foil as counter and reference electrode. The Lithium metal foil and MCMB are purchased from MSE supplies. Lithium bis(fluorosulfonyl)imide (LiFSI) has been purchased from TCI America. Dimethoxyethane (DME), Cyclopentyl Methyl Ether (CPME) were obtained from Sigma Aldrich. The commercial electrolyte used for comparison is made of 1M $LiPF_6$ in mixture of Ethylene Carbonate (EC) and Diethylene Carbonate (DEC) (1:1 v:v) battery grade from Sigma Aldrich. The electrolytes are prepared by dissolving necessary amount of salt in solvents in Argon filled glovebox. High mass loaded MCMB electrodes (6.2-6.3 mg cm^{-2}) are made at CAMP facility Argonne National Laboratory.

Structural Characterizations: The coordination structures of solutions were determined by a Raman microscope (Thermo Scientific DXR 2) with a 613 nm laser. The chemical composition on the surface of graphite electrodes were investigated by X-ray photoelectron spectrometer (Kratos AXIS Ultra) equipped with a monochromatized Al-Kα X-ray source. The electrodes were cycled 10 times in the suitable electrolytes for SEI formation and washed with dimethyl carbonate (DMC) in the Argon-filled glove box to remove the residual electrolyte components before the characterization of XPS.

Electrochemical Characterizations: The graphite electrodes with high mass loading is made consisting of mesocarbon microbeads (MCMB) graphite (91.83 wt. %) as an active material, C45 (2 wt. %) as a conductive agent, polyvinylidene difluoride (PVDF) (6 wt. %) as a binder, and oxalic acid (0.17 wt. %) as an additive were coated onto Cu foil with a mass loading of 6.2-6.3 mg cm^{-2} (CAMP Facility at Argonne National Laboratory (ANL). The electrode with less loading is made from blade coating in the laboratory with 80% MCMB powder, 10 wt. % carbon black and 10 wt. % polyvinylidene fluoride (PVDF) binder. The prepared electrode has an areal loading of 1.5 mg cm^{-2}. The electrodes were dried in vacuum oven at 80°C overnight and cut into 13 mm discs. The half cells were assembled using CR2032 coin-type cells with lithium metal as a counter electrode, a polypropylene membrane (Celgard 2500) as a separator and the prepared electrolytes in the Argon-filled glove box. The half-cell galvanostatic charge/discharge measurement was carried out using a battery-testing system (Arbin BT-2000) at a voltage range of 0.001 to 1.5 V versus Li/Li^{+}. Charging (lithiation) and discharging (delithiation) was performed in a constant current mode. To determine cycling stability at room temperature, the half cells were cycled at 0.5 C-rate (1C = 372 mA g^{-1}). For low temperature performance tests, the half cells were charged and discharged with the following C-rate at several temperatures (0.1 C for 0 °C, -10°C, -20 °C, and 0.005 C for -40 °C). The formation cycles were given for the cells at 0.1 C-rate for 5 cycles before all cycling tests. Rate capability tests were carried out with different current rates (0.2 C to 2 C) at room temperature. EIS were performed over a frequency range of 1 MHz to 50 mHz with 10 mV amplitude of AC voltage perturbation at several temperatures (25 to -20 °C). Before EIS, the half cells were cycled at 0.1 C for 1 cycle between 1.5 V and 0.001 V.

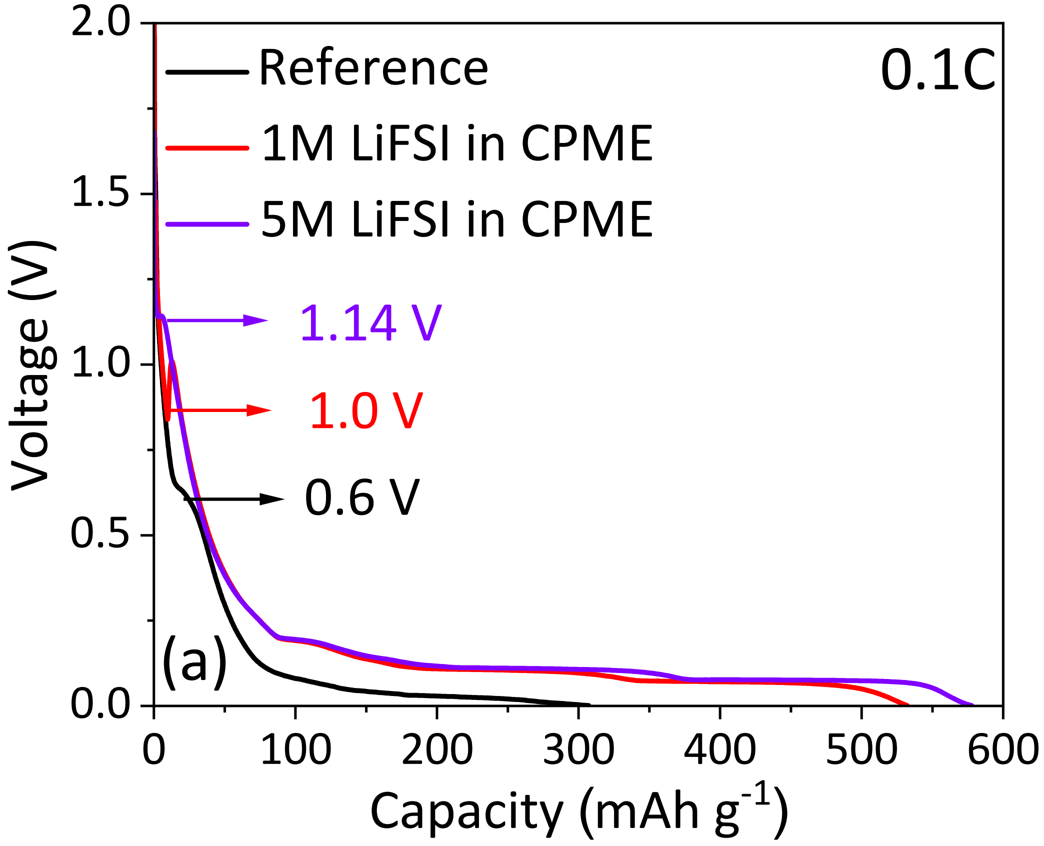


Fig. S1 First cycle discharge curves of graphite anode using three different electrolytes representing the formation of SEI layer.

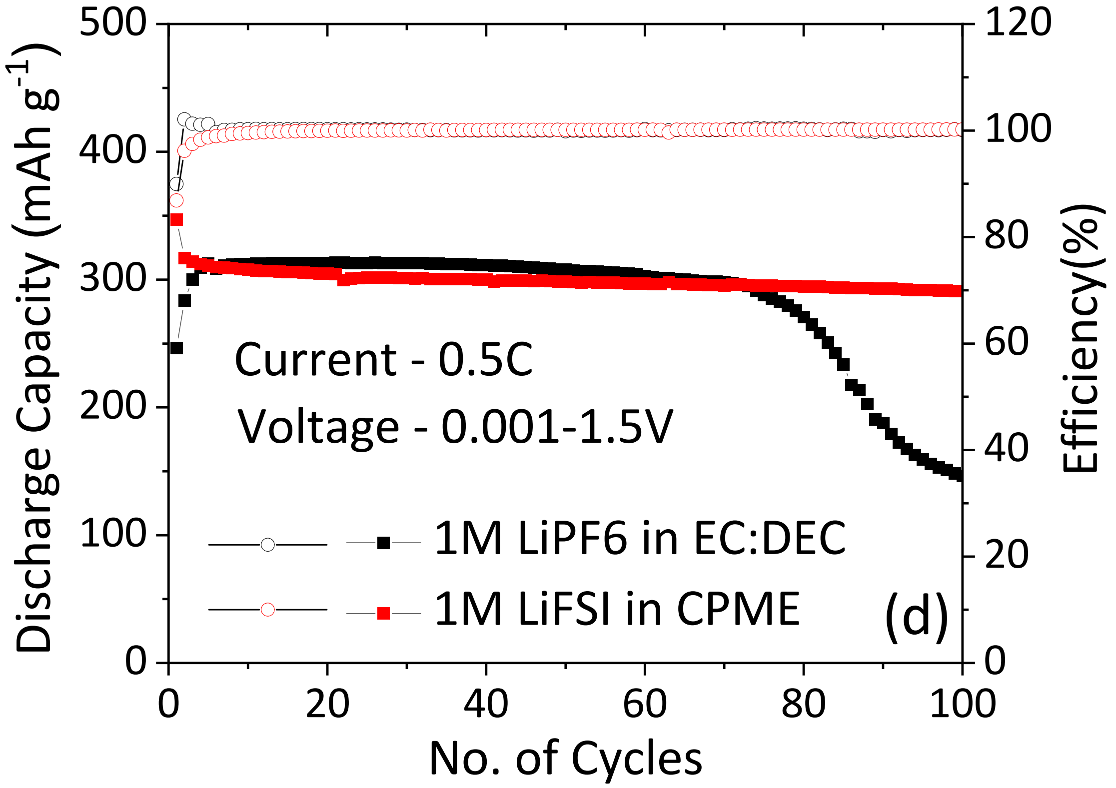


Fig. S2 Room temperature cyclability of high loaded graphite anode using 1M LiFSI in CPME electrolyte.

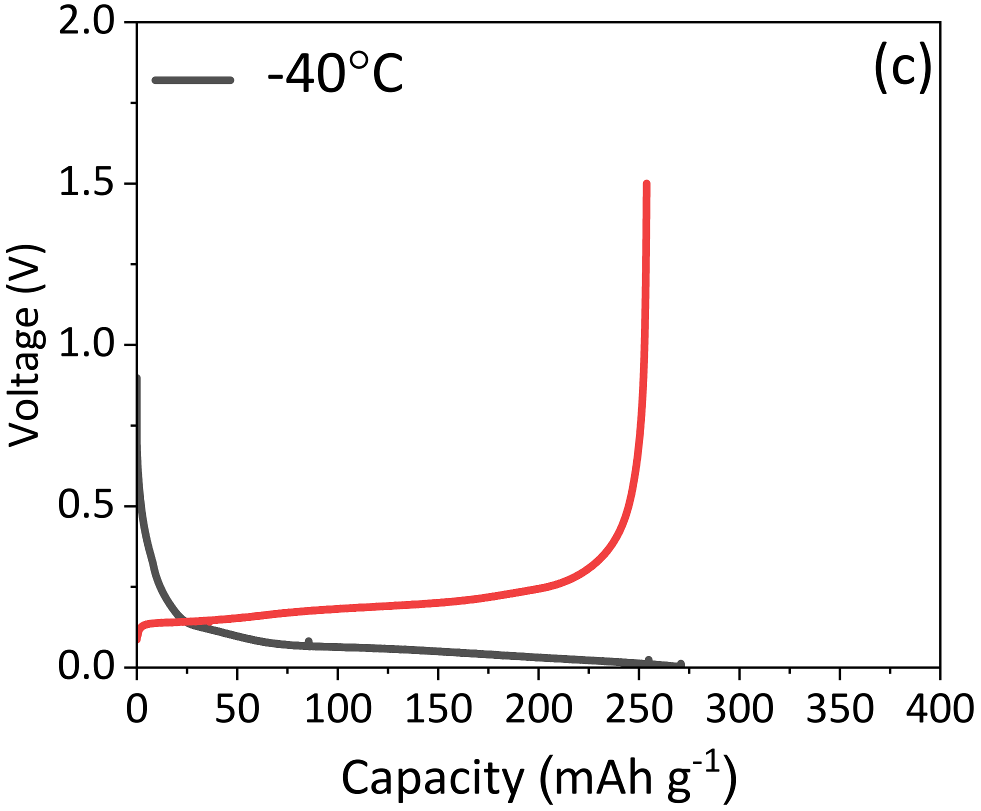
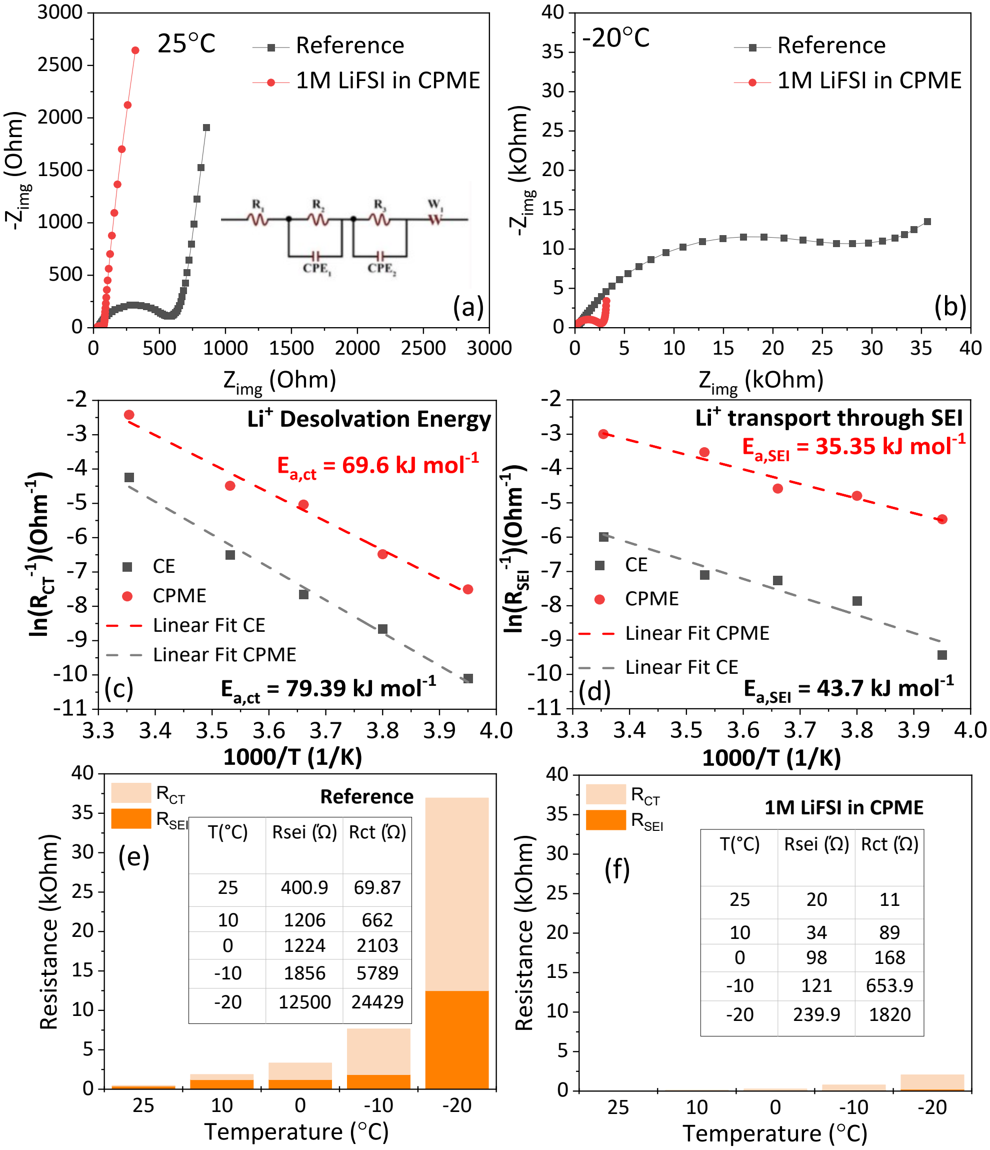


Fig. S3 Charge- Discharge curves of graphite anode using 1M LiFSI in CPME electrolyte at -40 ℃ at a current density of 0.005C.



Reference

T(°C)	Rsei (Ω)	Rct (Ω)
25	400.9	69.87
10	1206	662
0	1224	2103
-10	1856	5789
-20	12500	24429

1M LiFSI in CPME

T(°C)	Rsei (Ω)	Rct (Ω)
25	20	11
10	34	89
0	98	168
-10	121	653.9
-20	239.9	1820

Fig. S4. EIS spectra measured of commercial electrolyte and 1M LiFSI in CPME at **(a)** Room temperature and **(b)** low temperature **(c)** Arrhenius behavior of resistance corresponding to Li^+ desolvation **(d)** Arrhenius behavior of resistance related to Li^+ transport in SEI **(e and f)** Temperature dependent R_{ct} and R_{SEI} values of Reference and CPME electrolytes.

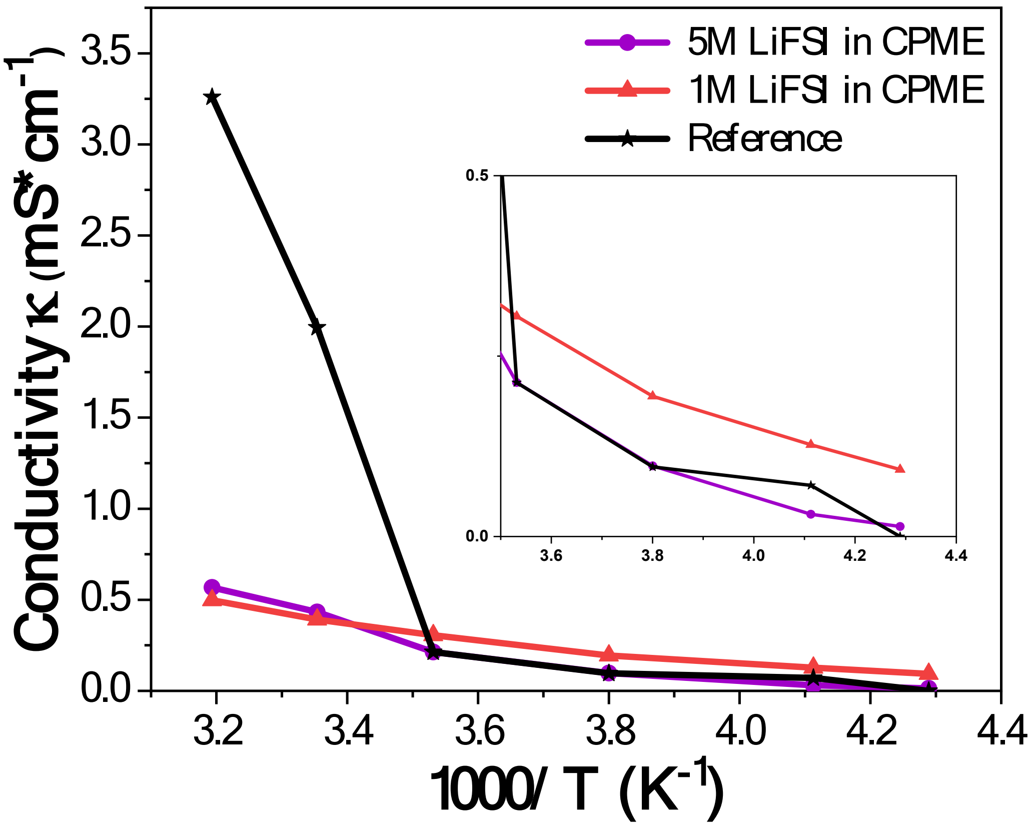


Fig. S5 Conductivity of three different electrolytes measured at different temperatures.

The conductivity of all three electrolytes were calculated at different temperatures of 40℃, 25 ℃, 10℃, -10℃, -30℃ and -40℃ and plotted in figure B. The corresponding values are provided in Table

$$k = \frac{\tau \quad l}{\emptyset_c R_s A}$$

Where k is conductivity of the electrolyte, $\emptyset_c$ is volume fraction of conducting element within the separator, τ is the tortuosity of the separator, l is the thickness of the separator (cm), A is the surface area of the SS, Rs is the resistance of electrolyte/separator. [1, 2] The reference electrolyte has higher ionic conductivity than the CPME electrolytes at room temperature, but with decreasing temperature, 1M LiFSI in CPME has the highest ionic conductivity than others. This justifies the superior low temperature performance at low temperature.

Temperature (℃)	**κ (mS/cm)**		
	Reference	**1M LiFSI in CPME**	**5M LiFSI in CPME**
40	3.26	0.497	0.567
25	1.995	0.392	0.433
10	0.213	0.305	0.213
-10	0.096	0.194	0.098
-30	0.071	0.127	0.031
-40	0	0.093	0.014

Table S1: Ionic conductivity values of three different electrolytes.

References:

[1] D. B. Shah, H. Q. Nguyen, L. S. Grundy, K. R. Olsen, S. J. Mecham, J. M. Desimone, N. P. Balsara, *Phys. Chem. Chem. Phys.*, **2019**, 21, 7857.

[2] D. P. Finegan, S. J. Cooper, B. Tjaden, O. O. Taiwoo, J. Gelb, G. Hinds, Dan. J. L. Bret, P. R. Shearing. *J. Power Sources*, **2016**, 333, 184-192.

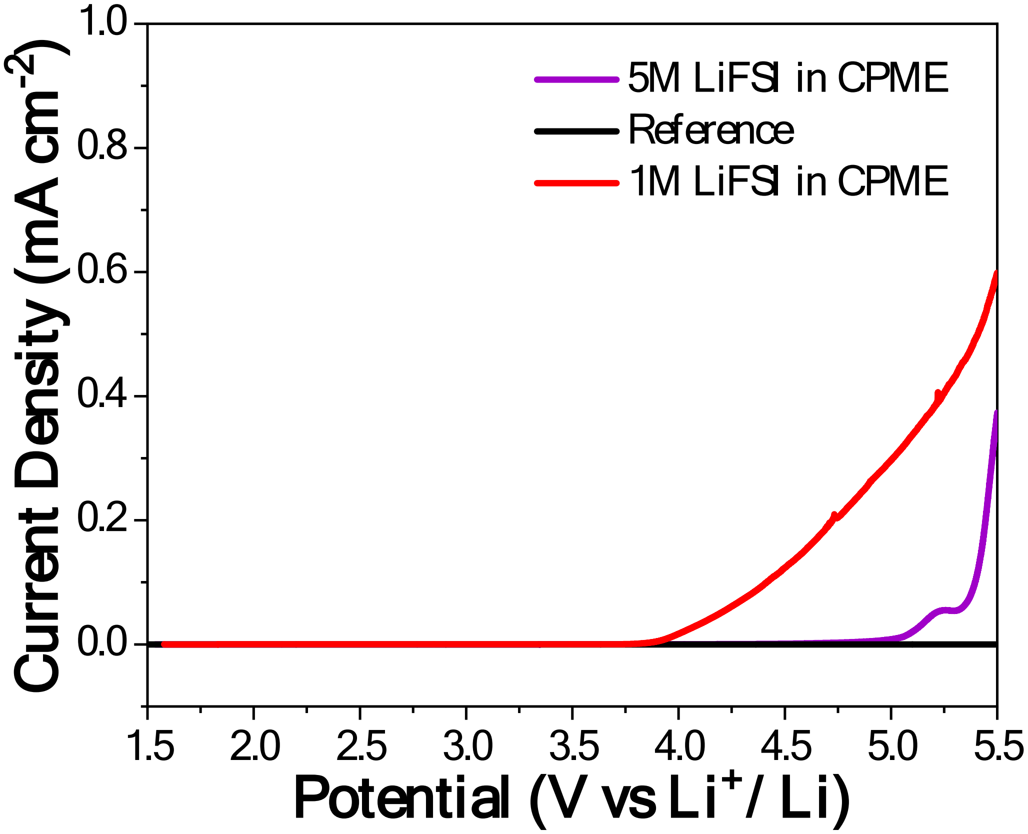


Fig. S6 The electrochemical stability of three electrolytes were conducted using LSV with Al working electrode and Li reference and counter electrode, sweeping from open circuit potential to 5.5 V at a rate of 0.5 mV s^{-1}.

We have added additional data about the CPME electrolyte using linear sweep voltammetry (LSV) and Ionic conductivity studies. The electrochemical stability of three electrolytes were conducted using LSV with Al working electrode and Li reference and counter electrode, sweeping from open circuit potential to 5.5 V at a rate of 0.5 mV s^{-1}. A very low background current is recorded for CPME electrolytes in the voltage range of 2.0 V to 3.6 V. The decomposition of 1M LiFSI in CPME starts at 3.7 V as seen in the obvious current flow. The 5M LiFSI in CPME has a modified solvation structure with better oxidation stability range due to the reduction in the free solvent molecules. The decomposition of this high concentration electrolyte starts at 4.5 V. The reference electrolyte with cyclic and linear carbonates has very good oxidation stability within the entire voltage range.

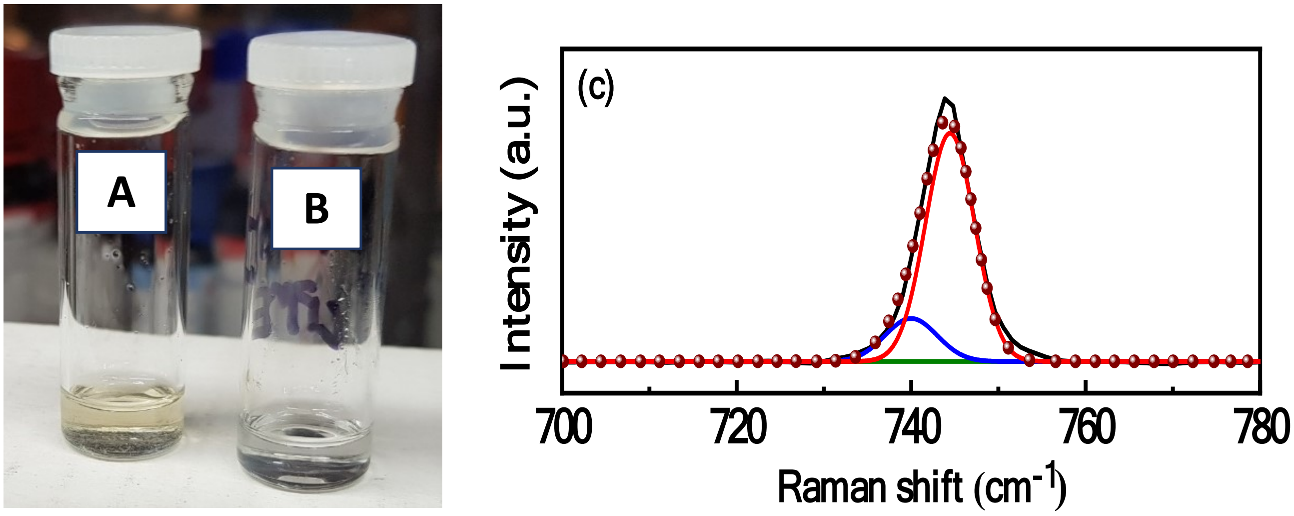


Fig. S7 (a) 1M $LiPF_6$ in CPME which is not completely soluble. (b) 1M LiTFSI in CPME with good solubility. (c) Raman spectra of 1M LiTFSI in CPME.

We prepared electrolytes using CPME solvent and 1M of different salts like LiPF6 and LiTFSI. It is found that 1M of $LiPF_6$ is not soluble in the CPME, while 1M LiTFSI is soluble in CPME. Hence, we provided the Raman spectra and voltage profiles of 1M LiTFSI in CPME measured at 1C rate. The Raman spectra shows the presence of CIP and Aggregates. The peak position of aggregates is at 744 cm^{-1}, which is lower than the LiFSI based electrolyte provided in Figure 1 and the area of the peak is significantly less. Hence, we could justify the advantages of using LiFSI in CPME electrolyte. The charge discharge is carried out at 1C rate and provided below in figure d. the reduction peaks are around 0.7 V, which is lower than the 1M LiFSI in CPME.

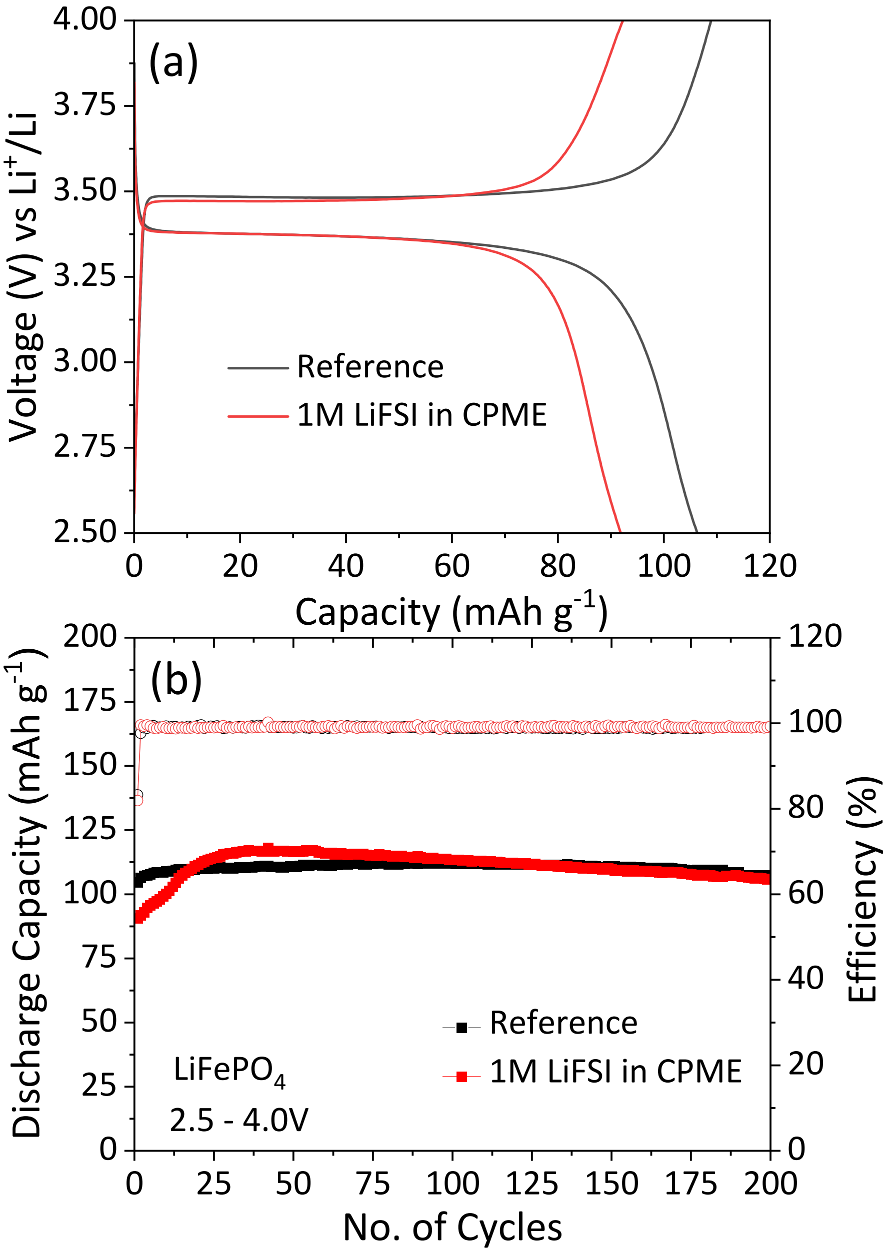

(a)
4.00
3.75
3.50
3.25
3.00
2.75
2.50
Voltage (V) vs Li$^+$/Li
0
20
40
60
80
100
120
Capacity (mAh g^{-1})
Reference
1M LiFSI in CPME
(b)
200
175
150
125
100
75
50
25
0
Discharge Capacity (mAh g^{-1})
120
100
80
60
40
20
0
Efficiency (%)
0
25
50
75
100
125
150
175
200
No. of Cycles
Reference
1M LiFSI in CPME
LiFePO$_4$
2.5 - 4.0V

Fig. S8 (a) Charge-Discharge curves and (b) Room temperature cyclability of $LiFePO_4$ half-cell using Reference and 1M LiTFSI in CPME at 1C rate.

we provided the half-cell data of the $LiFePO_4$ using Reference and 1M LiFSI in CPME. Figure **S8(a)** represents the charge discharge curve of the LFP/Li half-cell at 1C rate (170 mA g^{-1}) within 2.0-4.0 V. The initial capacity of the 1M CPME electrolyte (92 mAh g^{-1}) is lower than Reference (106 mAh g^{-1}). **Figure S8(b)** represents the cyclability of the cells with different electrolytes. The diluted CPME electrolyte has the same cyclability as that of the Reference electrolyte and indicates good performance.

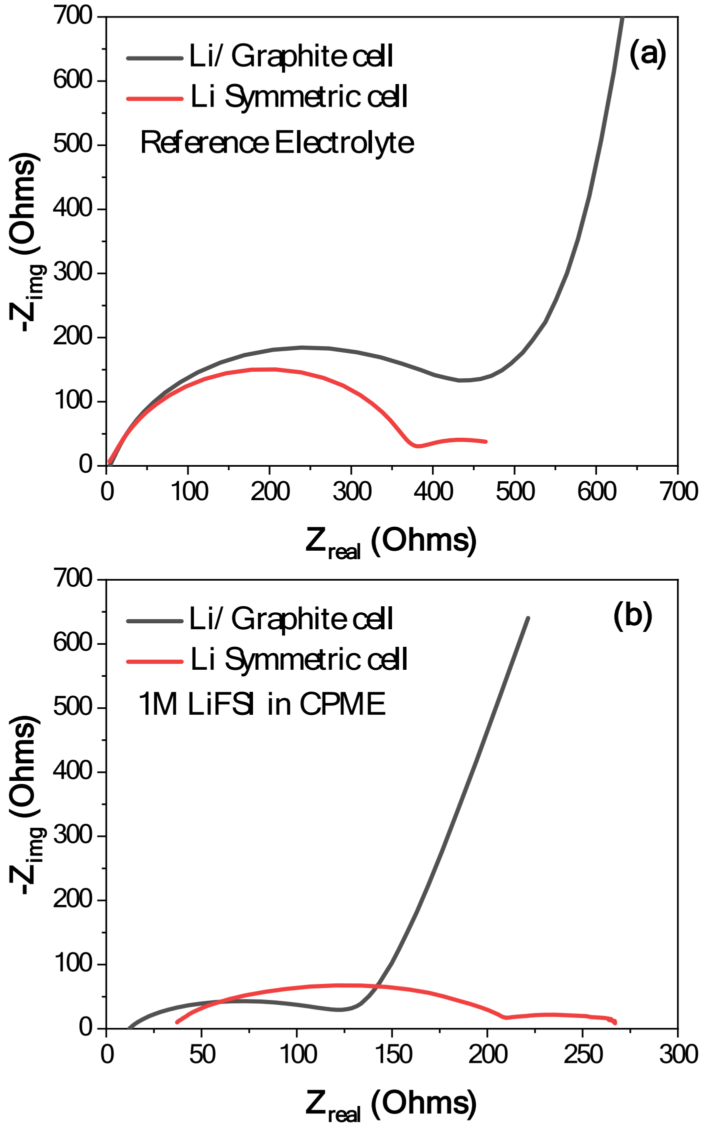


Fig. S9 EIS spectra of Lithium symmetric cell and Graphite half-cell using (a) Reference and (b) 1M LiFSI in CPME.

we did EIS of Li//Li symmetric cell and Graphite/Li half-cell, and the corresponding images are provided here. The reference electrolyte in **figure S9(a)** displays higher charge transfer resistance in both the configuration. This is due to the incompatibility of the carbonate electrolytes with lithium metal and graphite anode. Whereas the 1M CPME electrolyte (**figure S9(b)**) has low charge transfer resistance with graphite and lithium metal. This confirms the compatibility of this electrolyte with graphite.