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Supplementary Information

Enhancing Metallic Lithium Batteries Performance by Tuning Electrolyte Solution Structure

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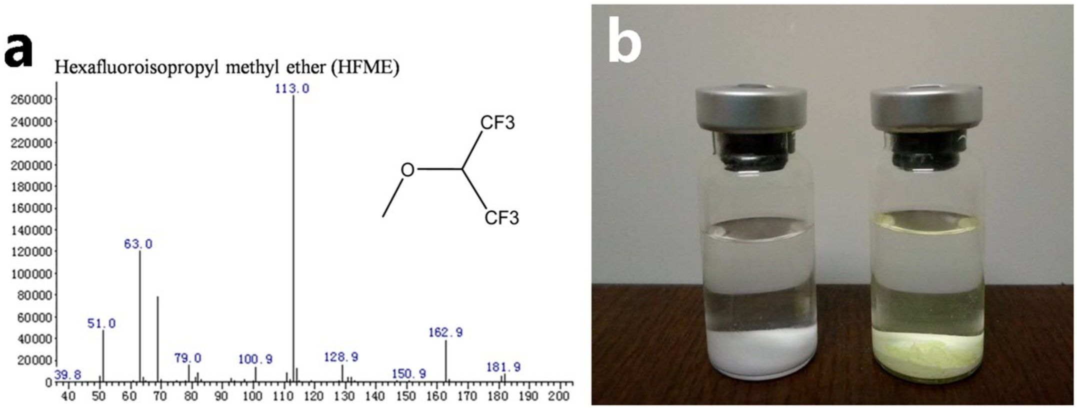

Fig.S1(a) The mass spectrum of HFME, (b) Photograph of LiFSI and Li$_2$S/S(1/7) in HFME.

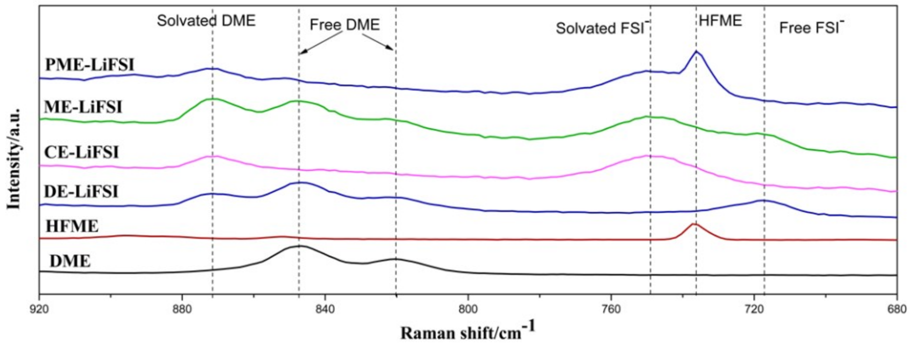

Fig. S2 Raman spectra of DME, HFME and different electrolytes. As shown, free DME (847.2 cm $^{-1}$ and 820.0 cm $^{-1}$) and free FSI$^-$ (718 cm^{-1}) are found in the medium concentration electrolyte, while the spectrum of the pseudo-medium concentration electrolyte is similar to that of CE-LiFSI, showing no free DME and free FSI$^-$ are found here. Therefore, this experimental results further prove that the salvation structure of Li$^+$ in PCE can be further strengthened by the introduced HFME.

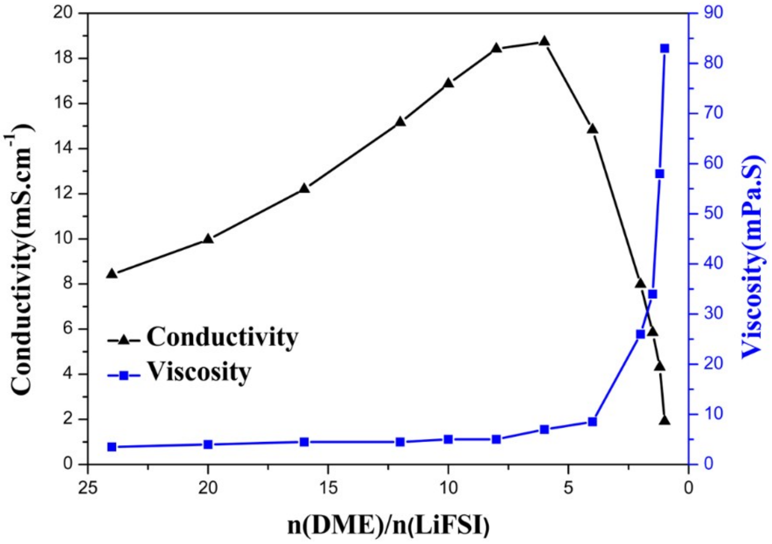

Fig.S3 Viscosity and ionic conductivity at room temperature for the different electrolytes. The conductivity of the DE (LiFSI: DME=1:10) is as high as16.87mScm^{-1}. And the viscosity increased to 82.6mpa.s from less than 10 mpa.S with the increased concentration. The conductivity of the concentrated electrolyte (LiFSI: DME=1:1) is as low as 1.74mS cm^{-1}, which is less than one half of the electrolyte (LiFSI: DME=1:1.2).

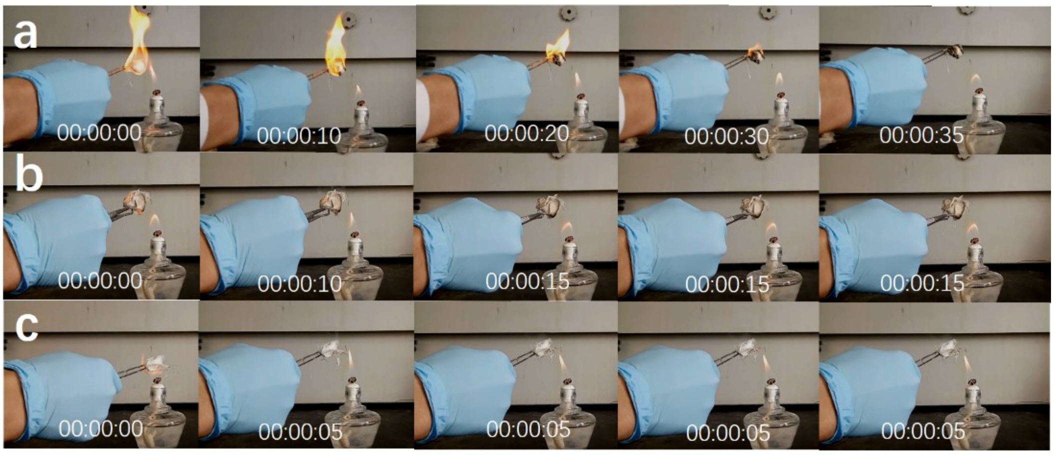

Fig. S4 Flame tests of (a) DE-LiFSI, (b)CE-LiFSI and (c) PCE-LiFSI. The self-extinguishing time of the dilute electrolyte is as long as 25S, which is much longer than that of the concentrated electrolyte(18S). Moreover, owing to the introduction of the non-flammable HFME (boiling point: 50.95 ^{o}C), the pseudo-concentrated electrolyte can’t be burn completely.

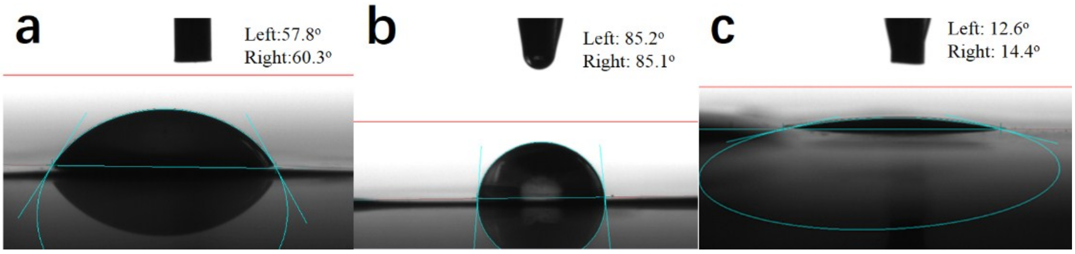

Fig. S5 Contact angle measurements of the electrolyte on the Celgard 2320 separator.(a) DE-LiFSI, (b) CE-LiFSI and (c) PCE-LiFSI.

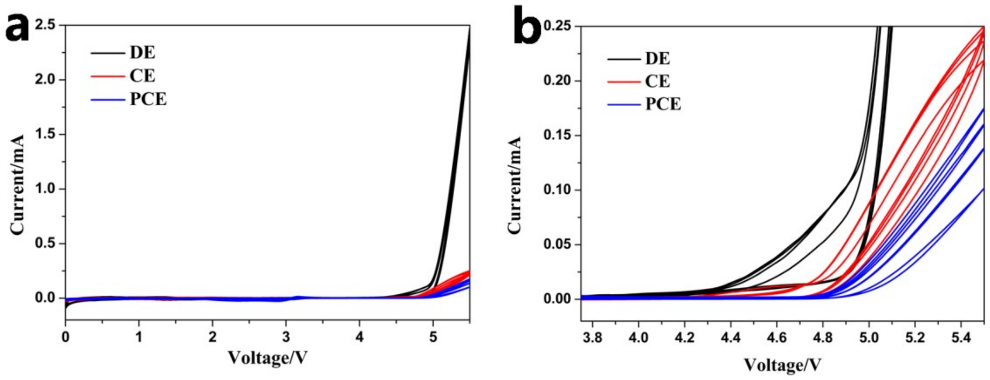

Fig. S6 Cyclic voltammograms on Pt with the differentelectrolytes,(b) The scaled datafrom the plots on the left. The scan ratewas 10 mV/s. The oxidative stability is improved originating from the unique solution structure of CE-LiFSI. All thesolvent coordinates to Li^+ in CE-LiFSI, electron donation occurs from thelone-pair at the oxygen atom of the solvent to Li^+ (a strongLewis acid), which remarkably lowers theHOMOlevel,raising its oxidation onset potential. The oxidative stability is further improved by PCE-LiFSI owing to the introduction of high stable HFME.

Fig. S7 Photograph of different pseudo concentrated electrolytes standing for 12 hours. Some lithium salt will be precipitated when the content of HFME is too high. Owing to the anti-solvent effect, some lithium will be precipitated when the content of HFME is too high[1, 2].

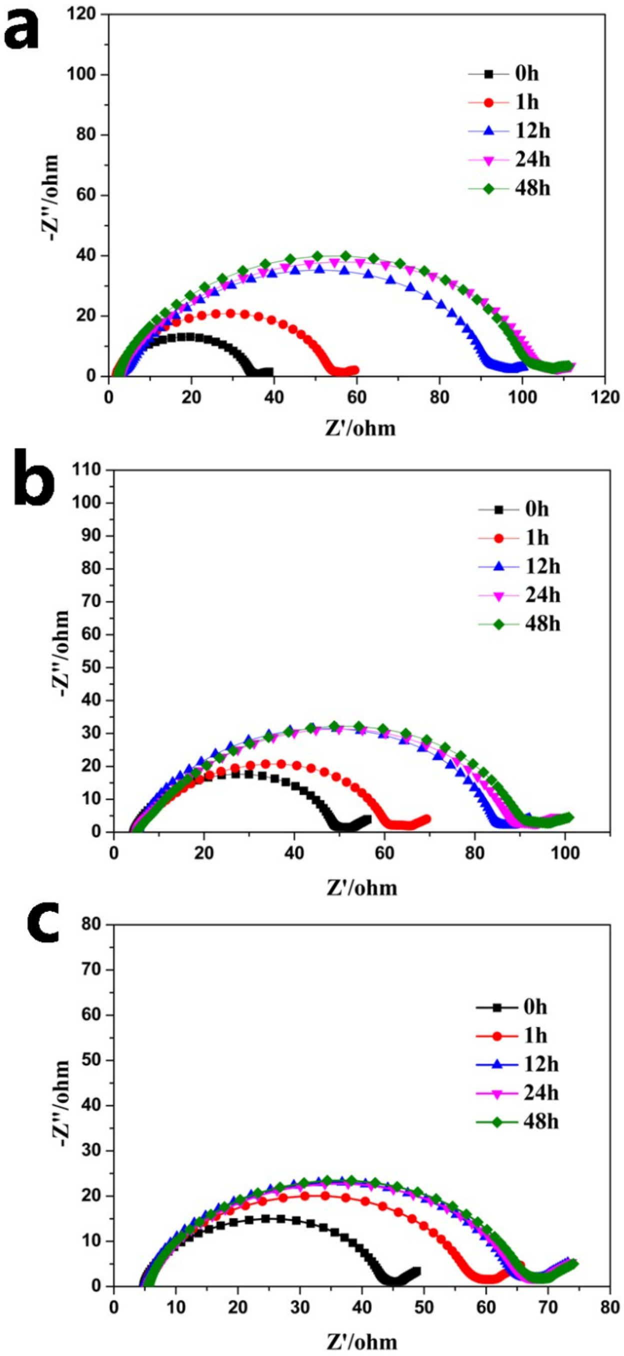

Fig. S8 Impedance spectra of Li|Li cells with different electrolytes upon standing for the indicated periods of time[3]. (a) DE-LiFSI, (b) CE-LiFSI, (c) PCE-LiFSI. The resistance of the cell does not change significantly for all the three electrolyte when these electrolytes are exposed to Li metal. The resistance of the cell in PCE-LiFSI is less than that of the cell in CE-LiFSI, showing a decreased polarization owing to the decreased viscosity and improved conductivity.

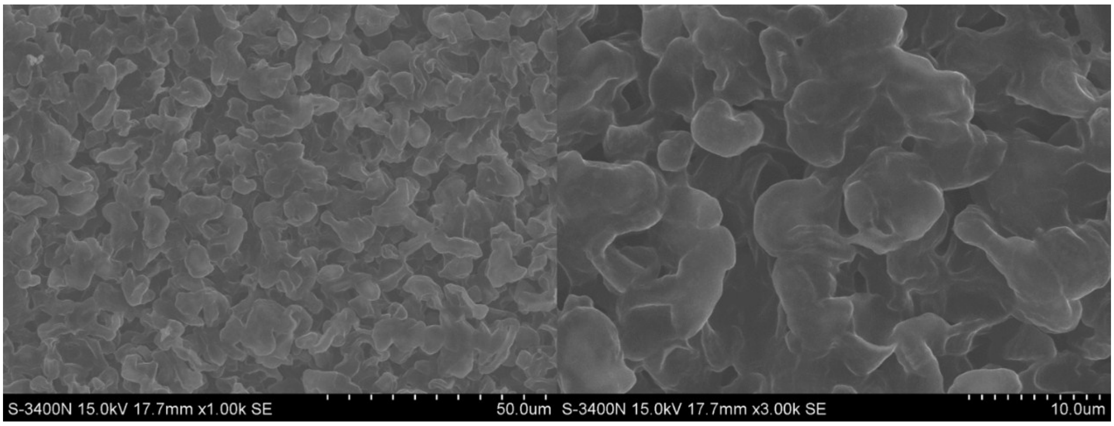

Fig. S9 SEM images of the morphologies of Li metal after plating on Cu substrates in DE-LiFSI.

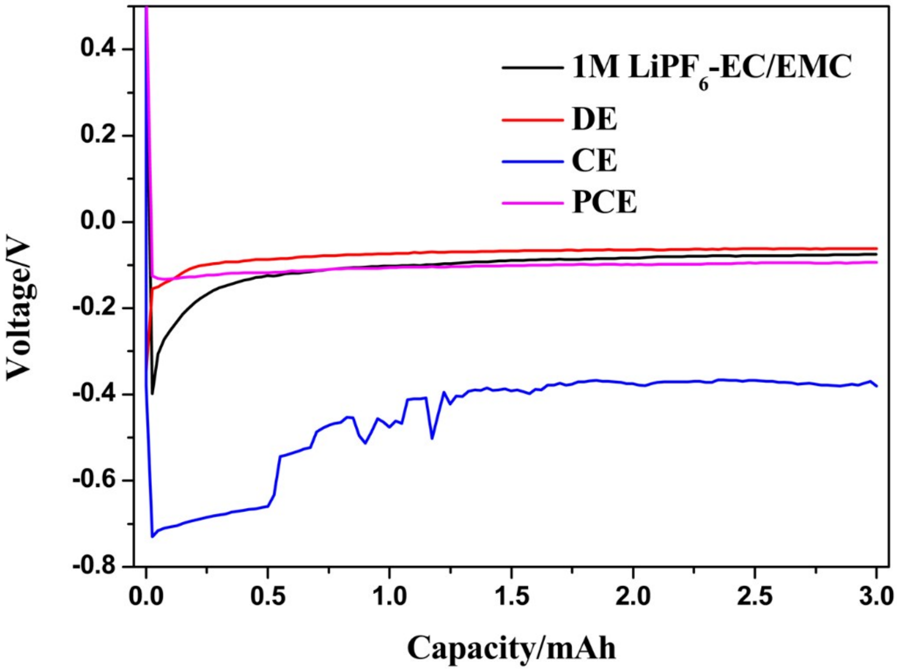

Fig. S10 Voltage profiles for the Li-Cu cellsplating in the different electrolyte.The plating voltage of Li-Cu cell in CE-LiFSI is as high as 0.7~0.4V, which is much higher than that of Li-Cu cell in PCE-LiFSI, showing a much decreased polarization.

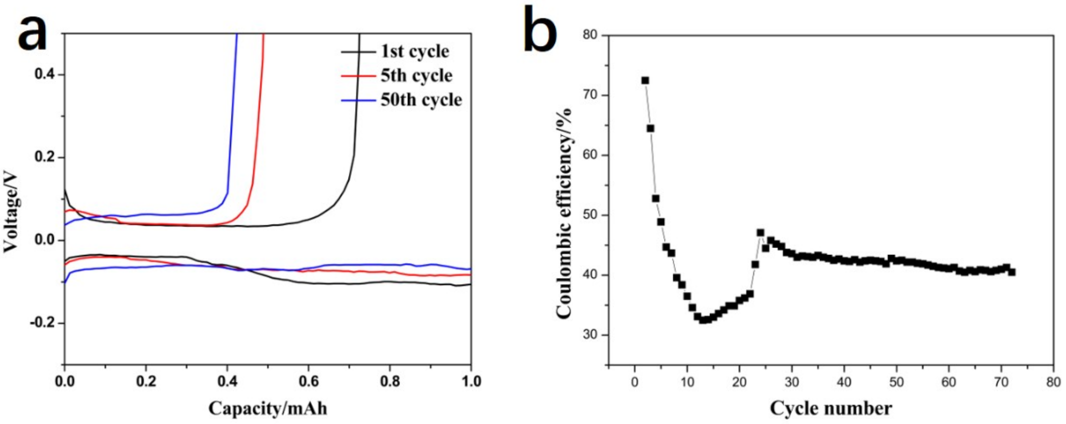

Fig. S11 (a) Voltage profiles and (b) coulombic efficiencies for Li-Cu cells cycles in 1M $LiPF_6$-EC/EMC electrolyte. The first coulombic efficiency of Li-Cu cell is only 73.7%, and it decreases to below 40% quickly, showing a poor lithium metal plating/stripping performance.

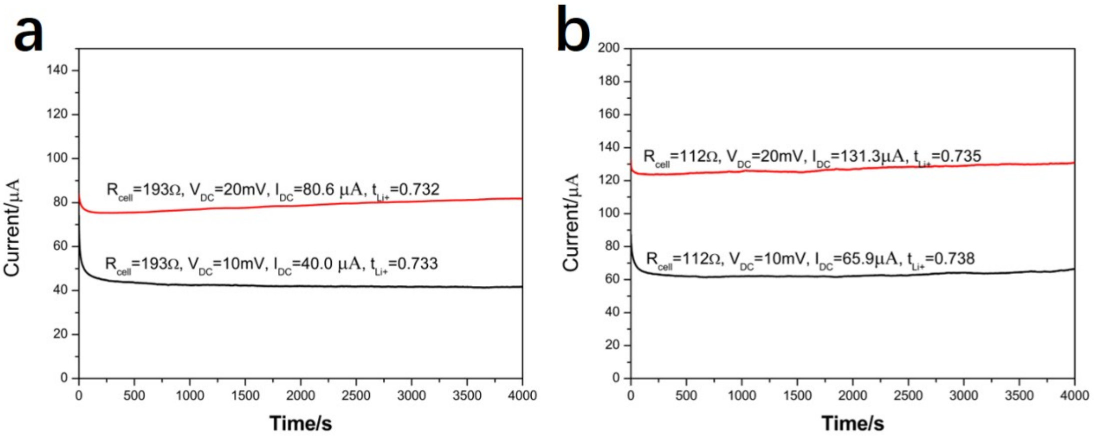

Fig. S12 The lithium-ion transference numbers of (a) CE-LiTFSI and (b) PCE-LiTFSI for different V_{DC} (10 mV and 20 mV). The lithium-ion transference numbers of PCE-LiTFSI doesn't show evident differences compared with those of CE-LiTFSI. Lithium-ion transference number $t_{Li+}=\sigma_{Li+}/\ (\sigma_{Li+}+\sigma_{TFSI-})$. The conductivity of specific ion is proportional to the concentration of mobile ion and its mobility. The mobility of an ion is determined by the viscosity of the medium and radius of mobile ion. In low-salt concentration electrolytes, lithium ions are coordinated with ether oxygen and form a large solvation shell compared with anions, leading to relatively lower mobility of solvated Li^+ cations. In CE and PCE systems, the number of solvated Li^+ cations is decreased and large anion ($TFSI^-$) could be more seriously dragged than the small unsolvated cation (Li^+) in this high viscosity system. Thus lithium-ion transference numbers of CE and PCE are as higher than that of DE.

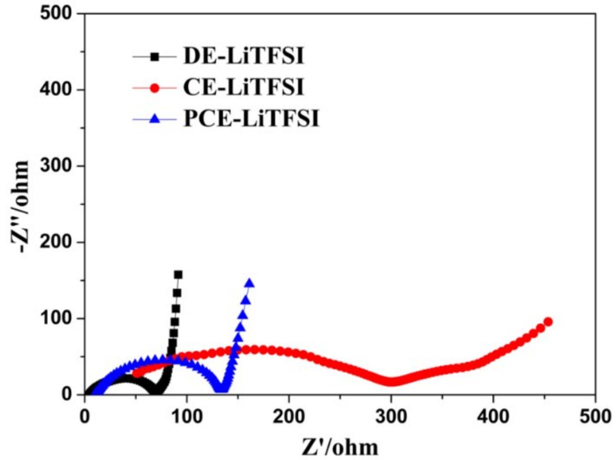

Fig.S13 Electrochemical impedance spectroscopy plots of Li-Scells in different electrolytes. The resistance value of the cell in the PCE-LiTFSI is only 135Ω, which is much smaller than that of the cell in CE-LiTFSI. This can be attributed to the increased conductivity, the decreased viscosity and good wettability between the PCE-LiTFSI and the electrode/separator.

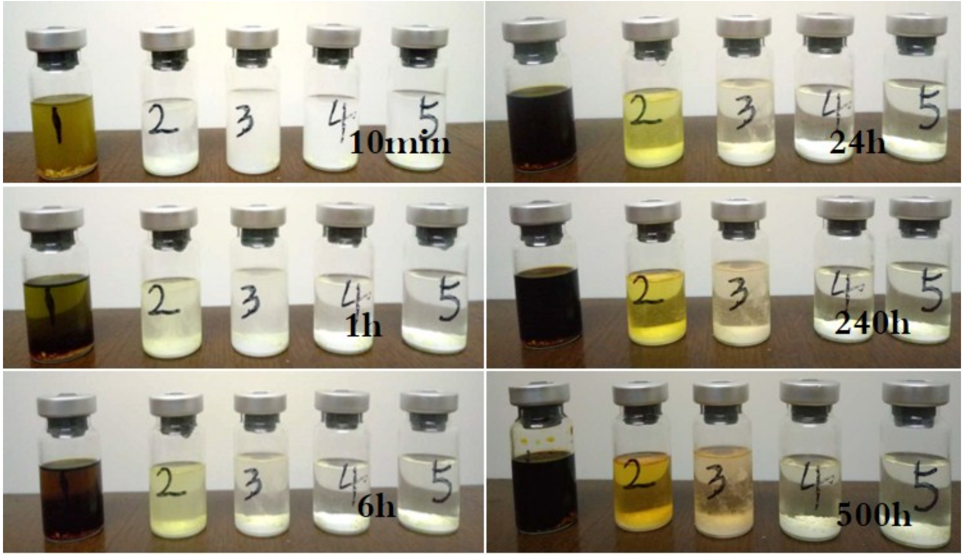

Fig.S14 The colour changes of three samples for different electrolytes containing the sameamount of Li_2S_8 along with time, (1-DE-LiTFSI, 2-SCE-LiTFSI, 3-SPCE-LiTFSI(HFME 40%)，4-SPCE-LiTFSI(HFME 50%), 5-SPCE-LiTFSI (HFME 60%)).

References

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