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Supplemental Information

Beyond concentrated electrolyte: further depleting solvent within Li^+ solvation sheath to stabilize high-energy-density lithium metal batteries

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EXPERIMENTAL PROCEDURES

Materials and Methods

All the chemicals employed in this synthesis section were purchased from Wako Pure Chemical Industries Ltd. without additional exception.

Preparation of different MOF composites

Preparation of the modified MOF composites:

(1) Synthesis of copper hydroxide nanorods (CHNs): Cupper hydroxide nanostrands (CHNs) were firstly synthesized by quickly mixing equal volume 1.16 g copper nitrate hexahydrate solution (300 ml) with 100 mg aminoethanol aqueous solution (300 ml) at room temperature and aged for 48 h. The CHNs composites were collected by filtering the mixture onto an organic membrane. Then, the CuBTC MOF was successfully obtained by immersing the CHNs film into 10 mM Benzene-1,3,5-tricarboxylic acid (BTC) water-ethanol (water/ethanol volume ratio 1:1, 40 ml) solution at room temperature for 12 h. The obtained composite was finally vacuumed at 180 °C for 72 h to generate the activated MOF sample.

(2) Synthesis of modified MOF (CuBTC-NSP): After the CHNs were obtained, 12 mg NSP (negatively charged sulfonate based polymer (Poly(sodium 4-styrenesulfonate), PSS) modified CuBTC MOF, also defined as CuBTC-PSS) was added into 300 ml CHNs solution to prepare the CHNs-NSP composites. Then the CuBTC-PSS MOF was prepared as same as that in the preparation process in Ms-9.0 from CHNs. The obtained modified MOF was finally vacuumed at 180 °C for 72 h to prepare the activated modified MOF sample.[S1]

Preparation of MOF film

MOF based solution was prepared by thoroughly mixing 90 wt. % activated MOF sample with 10 wt% Polytetrafluoroethylene (PTFE) in ethanol. The obtained MOF slurries were then quickly stirred to mix the sample evenly and evaporate the unnecessary organic solvent, finally resulting in sticky MOF putty. The obtained MOF putty was then uniformly spread on the Al foil and then dried at 80 °C for 10 min in drying oven. The MOF coated Al foil was then immersed into methanol for 5 min until the MOF film was detached from the Al foil and formed the flexible MOF film.[S2] The MOF film was then further compacted more than 10 tons of pressure to remove the inter-particle pores. The obtained MOF film was firstly dried at 80 °C for 1 hour in drying oven

and then followed by vacuumed dried oven at 180 °C overnight to activate the MOF film. The prepared activated MOF film was then cutted into small plates (16 mm in diameter) and re-activated under vacuum at 180 °C overnight before transferred into glove box for further usage.

Preparation of carbonate electrolyte.

Before this process, carbonate electrolytes (PC-LiTFSI) with different concentrations (1M and saturated) were firstly prepared. Typically, for the preparation of 1M PC-LiTFSI carbonate electrolyte, 2.87 g LiTFSI salt was mixed with 10 mL Propylene Carbonate (PC) solvent and stirred at 60 °C for 2 hours. Saturated carbonate electrolytes were prepared follow the same procedures except stoichiometric LiTFSI salt was added.

Preparation of the over-saturated carbonate liquid electrolyte (PC-LiTFSI with MOF).

The afore prepared activated MOF small plates were immersed into the 1M PC-LiTFSI electrolyte under 90 °C for 48 hours to soak electrolyte molecules into MOF channels. Then, the MOF plates filled with electrolyte were taken out, wiped with tissues followed by a physical press step and dried under a vacuum for 24 hours at 80 °C to get rid of any possible electrolyte solvents on the surface.

Synthesis of the 5.3 V-class $LiCoMnO_4$ composites

Firstly, 4.2 mmol $CoCl_2{\cdot}6H_2O$ and 3.5 mmol $MnCl_2{\cdot}4H_2O$ was dissolved in 132 mL of distilled water, and 4.9 g of urea, 5.0 g of ascorbic acid, and 4.0 g of polyvinylpyrrolidone (molecular weight 40K) were then added to the $CoCl_2/MnCl_2$ solution in sequence under stirring for 1 hour. After being stirred for 1 hour, the solution was transferred to a 100 mL Teflon-lined stainless-steel autoclave and maintained at 160 °C for 6 hours. The $CoMnCO_3$ microspheres were obtained after being centrifuged, washed with water and ethanol several times, and dried at 60 °C overnight. The obtained $CoMnCO_3$ microspheres were calcinated in air at 400C for 5 hours to obtain the $CoMnO_x$ microspheres. Then, 0.700 g of $CoMnO_x$ and 0.165 g of Li_2CO_3 were mixed and calcinated at 800 °C for 24 hours in an O_2 atmosphere to obtain the $LiCoMnO_4$ product.[S3] The synthesis process can also be simplified as follow: In fact, the LiCoMnO4 in this manuscript can be obtained followed by mixing $MnCO_3$, Co_3O_4 and $LiCO_3$ under a certain ratio. Specifically, the stoichiometric ratio among the three composites can be simplified as the ratio of Li: Co: Mn

elements. The ratio of Li: Co: Mn was 1.1: 1: 1. After a calcination process, the final 5.3 V-class $LiCoMnO_4$ can be obtained.

Electrodes Preparation

The obtained $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ (defined as NCM-811, provided by Prof An-Min Cao from Chinese Academy of Sciences (CAS)), the synthesized $LiCoMnO_4$ (defined as LCMO) and lithium foil (Lion Chemical Industry Co., Ltd.) were employed as electrode materials. Generally, 1.0 g electrode powders mixed with carbon black and polyvinylidene fluoride (PVDF, Du Pont-Mitsui Fluorochemicals Co. Ltd.) powder in a ratio of 8:1:1 and then directly stirring for 4 hours to get a viscous solution. The obtained slurry was then homogeneously coated onto Al foil current collector by a scraper. After tiny pressing procedure, the active materials-loaded Al foil was vacuum dried at 110 °C overnight. Part of the obtained cathode was cutted into final electrode plates (11 mm in diameter), and the mass loading of the NCM-811 and LCMO cathode materials were about 9.2-9.4 mg/cm^2 for full cells.

Cell Assembly and Electrochemical Measurements

CR2032 coin cells were assembled in an argon-filled glove box, in which both the moisture and oxygen contents were controlled to be less than 1 ppm. The prepared over-saturated carbonate electrolyte (PC-LiTFSI with MOF) was closely attached to the high-voltage cathodes and followed by a physical pressing process. The obtained cathode and electrolyte was then physically pressed on the surface of Li anode and then placed in the coin cell for cell assembling. For comparisons, cells using conventional carbonate electrolytes (1M PC-LiTFSI without MOF, 70 μL) were also assembled accompanied with the glass fiber as separators. The NCM-811//Li cells were operated with a potential limit between: 2.7-4.4 V in the study. The LCMO//Li cells were cycled between 3.0-5.3 V in this paper. Before each electrochemical characterization, the cells were kept on open circuit for 10 hours. All of the potentials in this study were referenced to Li/Li^+. For 2032 coin-type cells, the galvanostatic electrochemical measurements were carried out under potential control using the battery tester system HJ1001SD8 (Hokuto Denko) at 25 °C. For the Linear sweep voltammetry (LSV), PITT, EIS and CV tests, the electrochemical experiments were carried out under the control of a potentiostat (Potentiostat/Galvanostat PGSTAT30, Autolab Co. Ltd., Netherlands) at room temperature. The current and potential outputs from the potentiostat were recorded by a multifunction data acquisition module/amplifier (PGSTAT30 Differential

Electrometer, Autolab), which was controlled by General Purpose Electrochemical Software (GPES). For the specific test conditions, we will show them in their corresponding sections in related supplementary figures. The ionic conductivity was measured by a symmetric coin cell with two stainless steel electrodes. To test the ionic conductivity of the diluent and saturated LiTFSI-PC electrolytes, Glass Fiber (GF) wetted by electrolyte was sandwiched between two stainless steel sheets. The "solvent-depleted electrolyte" was sandwiched between two stainless steel sheets. Noted that to make sure the "solvent-depleted electrolyte" was successfully formed, we harvested the MOF layer with "solvent-depleted electrolyte" from a cycled (5 cycles) "solvent-depleted electrolyte" used Li//Li half-cell by physically peel off the MOF layer coated on the electrode. After the "solvent-depleted electrolyte" was successfully obtained, it is hence can be used as membrane to sandwiched between two stainless steel sheets for ionic conductivity test. We used an exhaustive stripping of Li metal method in a Li//Cu cell with excess Li to identify the amount of Li loss during Li cycling and calculate the corresponding coulombic efficiency. In this method, a given amount of charge (Q_T) is used to deposit Li onto the Cu substrate first as a Li reservoir, then a smaller portion of this charge (Q_c) (For cell used one time excess Li, 4 mAh/cm^2 Li was pre-deposited on Cu current collector, then the Li//Cu cell was discharged/charged at current rate of 1 mA/cm^2 for 2 hours, respectively; For cell used two time excess Li, 6 mAh/cm^2 Li was pre-deposited on Cu current collector, then the Li//Cu cell was discharged/charged at current rate of 3 mA/cm^2 for 2 hours, respectively) is used to cycle Li between working and counter electrodes for N cycles. After N cycles, a final exhaustive strip of the remaining Li reservoir is performed to the cut-off voltage. The final stripping charge (Q_S), corresponding to the quantity of Li remaining after cycling, is measured. The average CE over N cycles can be calculated by simple mathematical calculation.

Morphology and Structure Characterization

SEM, XRD, TEM and XPS Characterizations

The morphology of the as-prepared MOF products, pristine cathodes and cycled cathodes and Li anodes were characterized with scanning electron microscopy (SEM, JEOL JSM-6380LV FE-SEM). Moreover, the cycled NCM-811 and LNMO cathodes were also characterized with transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN). X-ray photoelectron spectroscopy (XPS) was performed using a VG scientific ESCALAB 250 spectrometer with

monochromic Al Kα excitation (1486.6 eV). X-ray diffraction (XRD) measurements were performed on a Bruker D8 Advanced diffractometer fitted with Cu-Kα X-rays (λ =1.5406Å) radiation at a scan rate of 0.016 °/s. For the pre-treatment procedures: The cycled cells were transferred into an Ar glove box once the electrochemical treatments were finished, and the electrodes were extracted from the cell and placed in a glass bottle. The electrode plates were twice rinsed by dimethoxyethane (DME, Sigma Aldrich, 99%) to wash off the electrolyte salt and the residual solvent, and then evaporated in a vacuum chamber, connected to the glove box, for 12 hours. The dried electrode plates were moved back to glove box and placed onto a SEM or XPS sample holder. The sample holder was sealed in an airtight container and then transferred into the SEM or XPS sample loading chamber. Note that, in order to restrain the exposure time to the ambient, samples (cycled electrode plates) were tightly sealed into a glass bottle (fill with Ar gas), and transferred to the related chambers (SEM and XPS) as quickly as possible. Thus, we assumed the morphology and the component of electrode surface would not obviously change for such a short time exposure to the open air.

Nuclear Magnetic Resonance (NMR) Spectroscopy Characterizations

The NMR spectra were recorded using a spectrophotometer (500 MHz Ultra-ShieldTM, Bruker). Typically, 256/128 ($^{1}H/^{19}F$) times were accumulated for one spectrum. The electrodes and separators were extracted from the cycled cells without further pretreatment. 750 μL of D_2O (99.9 atom % D, Wako Chemicals) was used to extract the residual electrolyte and soluble parasitic products (mainly carboxylates and fluorides) from the electrodes and the separators, then the solution was transferred to septa-sealed NMR tube. To quantify the amount of related components, 1 μL of benzene (C_6H_6, Sigma Aldrich, 99%) and 1 μL of fluorobenzene (C_6H_5F, Sigma Aldrich, 99%) were mixed and injected through the septa and employed as an internal standard. The method here was very similar as the ones introduced in our previous works.[S4]

Spatial resolution Operando-Raman Spectroscopy Characterizations

The Raman spectra were recorded using a JASCO microscope spectrometer (NRS-1000DT). The spectral resolution of the Raman spectra in the study was ca. 1.0 cm^{-1}. Typically, the scattering signal in Raman spectrum was weak and hard to be investigated. In this case, in order to obtain strong and clear peaks on the spectra, we took advantage of a shell-isolated nanoparticle-enhanced Raman spectroscopy (SHINERS) technique that evidently enhances the scattering signal.[S5, S6]

Briefly, Au nanoparticles (NSp) were synthesized with a diameter of 30~40 nm as core by a standard sodium citrate reduction method. Then freshly prepared aqueous solution of 1 mM (3-aminopropyl) trimethoxysilane (APS, Sigma Aldrich) was added to the gold sol under vigorous magnetic stirring for 15 minutes, followed by the addition of a 0.54 wt % sodium silicate solution (Tokyo Chemical Industry Co., Ltd). Then, the solution was heated to 90 °C under vigorous magnetic stirring for 1 hour. The series of steps ensures the formation of an ultra-thin SiO_2 shell (2-4 nm) without any pinhole. The washed and dried Au@SiO_2 NSp were re-dispersed in ethyl alcohol. Finally, the obtained Au NSp solution was mixed with MOF particles together with NMP as solvent before the NSp contained MOF was coated on the surface of NCM-811 cathode for Raman experiment. These Raman samples were further dried in vacuum at 80 °C for 18 hours before assembled into the cell. Note that the amount of deposited NSp was very small, so that we assumed it would not cause any influence on the electrochemical behaviors.

FT-IR Characterizations

Fourier-transform infrared (FTIR) Characterizations

FTIR measurements were carried out on a FT/IR-6200 spectrometer (JASCO Corp.). Typically, 64 interferograms were accumulated for one spectrum with a resolution of 4.0 cm^{-1}. For pretreatment, the cycled cells were transferred into an Ar glove box once the discharge finished, and the cathodes were extracted from the cell and twice rinsed by dimethoxyethane (DME, Sigma Aldrich, 99%) to wash off the electrolyte salt and the residual solvent, and then evaporated in a vacuum chamber, connected to the glove box, for ~15 min. The dried cathode was scratched off (nearly 1×2 mm^2) and then grounded together with potassium bromide (KBr, FTIR grade, purity of >99 %, Sigma Aldrich). The KBr powder was dried in vacuum at 100 °C for 24 hours before using, and the grinding procedure was carried out in an Ar-filled glove box. The mixture powder was pressed into hyaline pellets in vacuum under high pressure (4.0 Mpa) for 5 minutes. For the characterization of electrolyte solution, the cycled electrolyte was uniformly coated onto the KBr pellet in Ar-filled glove box. The KBr-based pellet was sealed in an airtight container and then rapidly transferred into the IR sample loading chamber, in which continuously purged with inert argon gas. The PSS and the prepared CHNs, CHNs-PSS, CuBTC and CuBTC-PSS composites were tested using the common FT-IR following the aforementioned experiment procedures.

Etching Fourier-transform infrared (FTIR) Characterization

For pretreatment, the cycled cells were transferred into an Ar glove box once the discharge finished, and the cathodes were extracted from the cell and twice rinsed by dimethoxyethane (DME, Sigma Aldrich, 99%) to wash off the electrolyte salt and the residual solvent, and then evaporated in a vacuum chamber, connected to the glove box, for ~15 min. The washed cycled cathodes were attached on the plate of etching IR instrument. And the IR spectra were collected with 2 seconds as interval. As a result, 25 points were recorded. The cycled NCM-811 cathode used over-saturated carbonate electrolyte (1 M PC-LiTFSI with MOF) and the cycled NCM-811 cathode used common carbonate electrolyte (1 M PC-LiTFSI without MOF) were tested using the etching FT-IR following the aforementioned experiment processes.

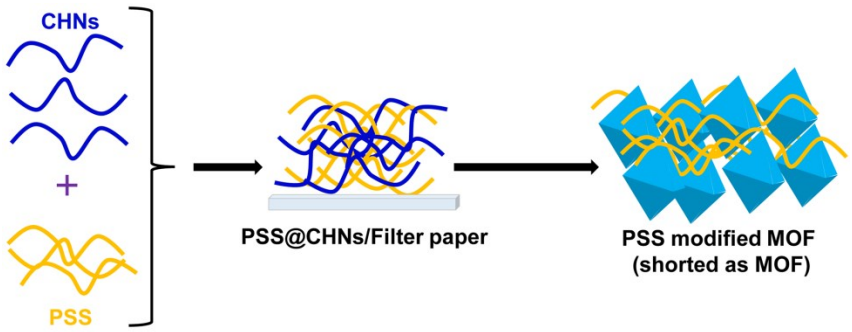

Figure S1. The schematic illustration for the preparation process of the channel modified MOF.

After the Cupper hydroxide nanostrands (CHNs) were synthesized, negatively charged sulfonic polymer (poly(styrenesulfonate), PSS) was added and adsorbed on the surface of the CHNs and forming CHNs-PSS composites. By using in-situ solid confinement conversion method, after the 1,3,5-Benzenetricarboxylic Acid (H_2BTC) was added, Cu ions contained in the form prepared CHNs-PSS coordinated with the organic ligand quickly and formed a MOF with PSS trapped inside its channels.

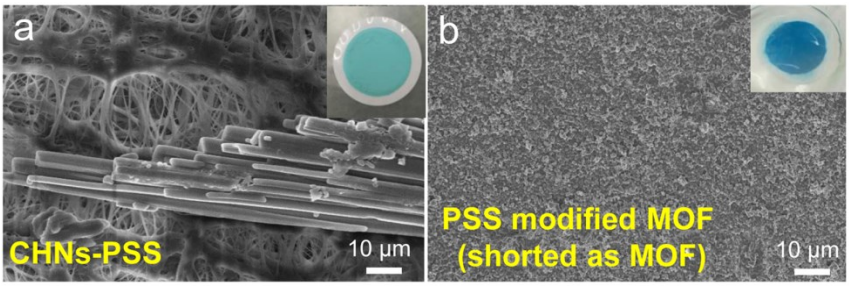

Figure S2. SEM of the CHNs-PSS for the synthesis of the modified MOF.

The color changes from light blue to dark blue suggests the CHNs-PSS were successfully transformed to PSS modified MOF, which was also verified by the corresponding apparent SEM morphology changes.

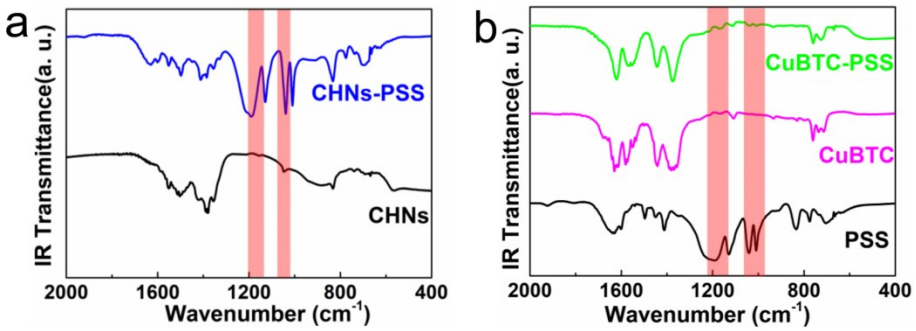

Figure S3. FT-IR spectra of the PSS and the prepared CHNs, CHNs-PSS, CuBTC and CuBTC-PSS composites.

The FT-IR spectra of the CHNS-PSS and CuBTC-PSS (MOF) jointly evidence the PSS was successfully incorporated into channels of CuBTC-PSS (MOF). Moreover, compares with the pristine NSP, the slightly positive peak shift of the sulfonate groups in CuBTC-PSS (MOF) demonstrates the interactions between PSS and nude Cu sites inside CuBTC-PSS (MOF) channels.

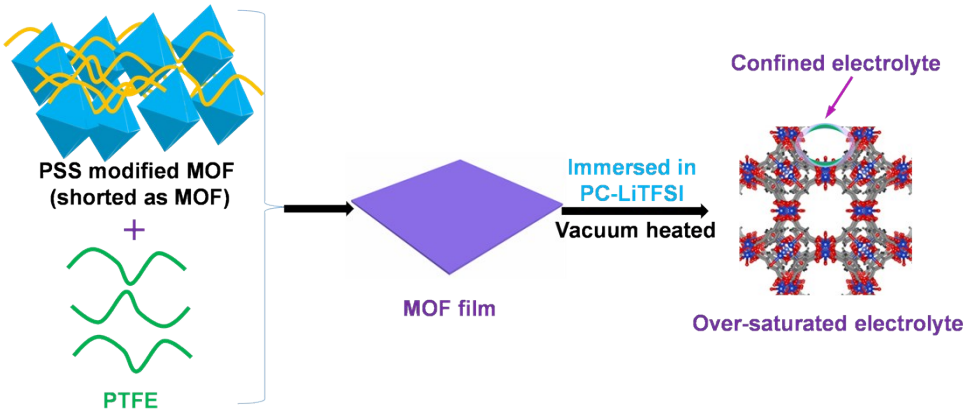

Figure S4. The schematic illustration for the preparation process of the MOF film.

The afore-prepared MOF composites were then physically mixed with Polytetrafluoroethylene (PTFE) to prepare flexible MOF films. Noting that before immersed in 1M PC-LiTFSI carbonate electrolyte, the obtained MOF films were under a vacuumed heat-treatment to activate the MOF films (vacuum heated at 180 °C to remove moisture within MOF cavities). The activated MOF can facilitate the infiltration of electrolyte.

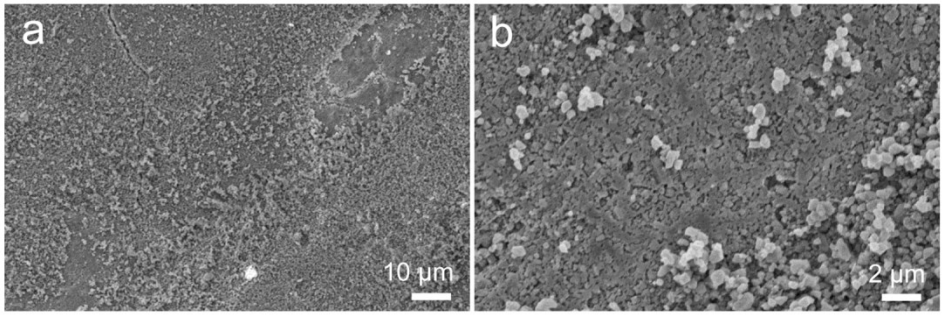

Figure S5. SEM images of the prepared MOF film.

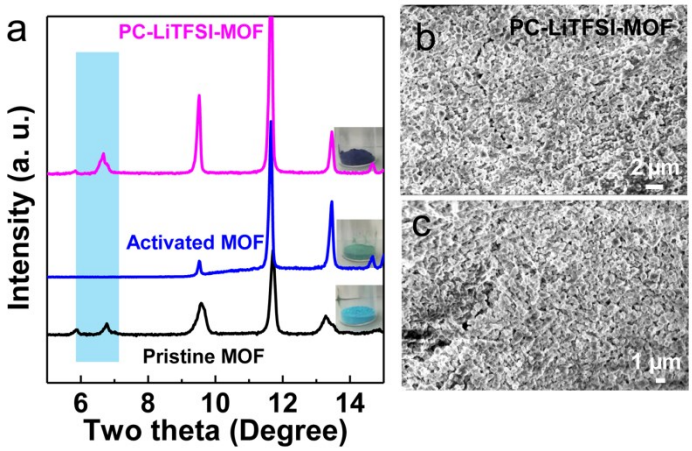

Figure S6. Physical characterizations of the prepared solvent-depleted electrolyte (PC-LiTFSI with MOF). (a) XRD patterns of the pristine MOF powder, the activated MOF powder (vacuum activated at 180 °C) and the activated MOF after immersed in PC-LiTFSI (solvent-depleted electrolyte, PC-LiTFSI with MOF) (The inset shows corresponding color changes of the three different samples). (b, c) SEM images of the prepared solvent-depleted electrolyte electrolyte (PC-LiTFSI with MOF).

The (111) peak disappears (light blue triangle highlighted, indicates the coordination status of water molecules on Cu metal sites inside MOF channels) after the activation process and reappears after incorporating with PC-LiTFSI (followed by filtration and removal of any excessive solvent). These characteristics together indicate the removal of the coordinated water molecules (blue curve) and binding of the Cu metal sites with electrolytes, respectively, which was also verified by the apparent color changes (from light blue to dark green and final dark blue).

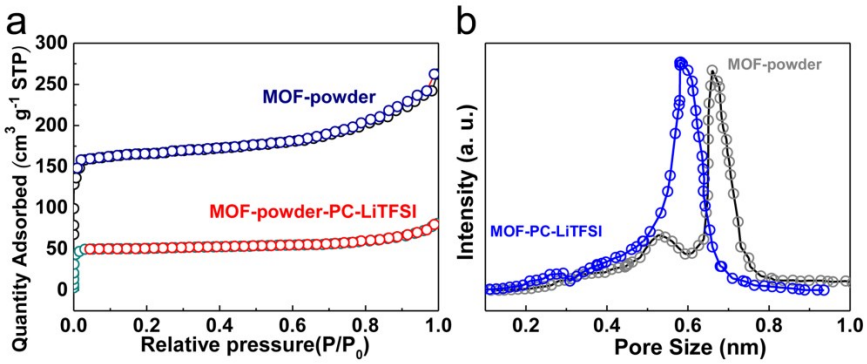

Figure S7. N_2 adsorption/desorption isotherms of and pore size distribution of the over-saturated carbonate electrolyte (PC-LiTFSI with MOF).

The apparently decreased BET surface area and decreased pore size distribution together indicates the successful incorporation of electrolyte into the pores of the MOF and finally leading to the formation of solvent-depleted electrolyte (PC-LiTFSI with MOF) with narrowed pore sizes compares with its pristine MOF counter-part.

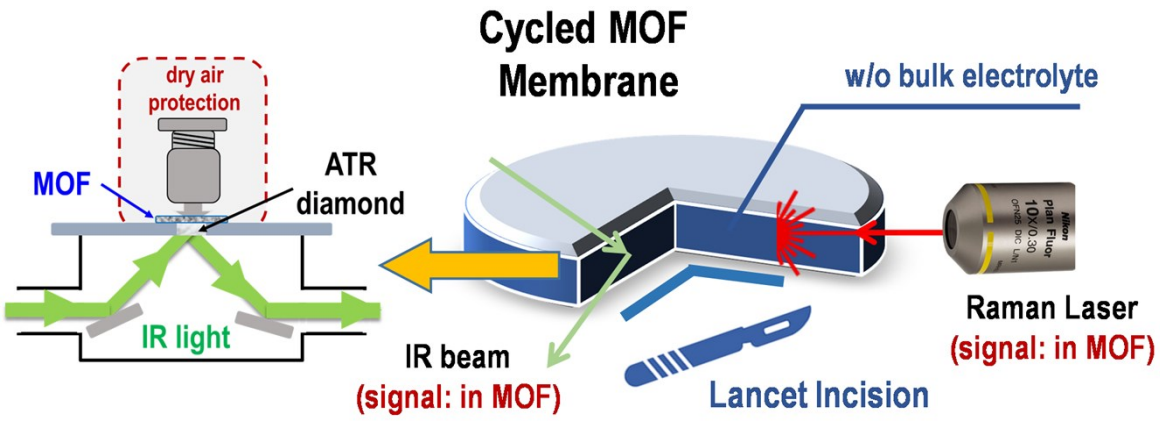

Figure S8. Schematic illustration of the operando-Raman and ATR-FTIR characterization system employed in this study.

Typically, the scattering signal used in common Raman spectroscopy was relatively weak, therefore, in certain circumstances, for certain samples, it is extremely hard to collect useful signals. To collecting strong and clear peaks, a SHINERS (shell-isolated nanoparticle-enhanced Raman spectroscopy) technique that greatly enhances the intensity of scattering signal was adopted. Points from MOF were selected for the operando-Raman and ATR-FTIR test to study the configuration of electrolytes confined inside MOC channels.

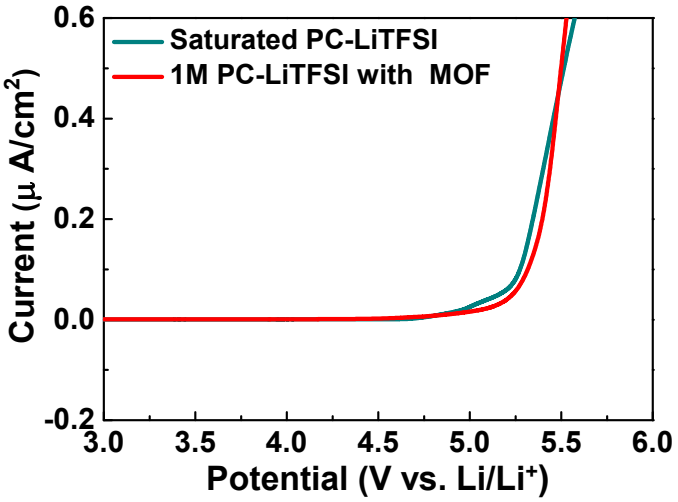

Figure S9. LSV curves of the conventional saturated PC-LiTFSI and the prepared (solvent-depleted electrolyte (1M PC-LiTFSI with MOF).

Clearly, even compared with saturated electrolyte, our prepared solvent-depleted electrolyte (1M PC-LiTFSI with MOF) still exhibits higher oxidation stability.

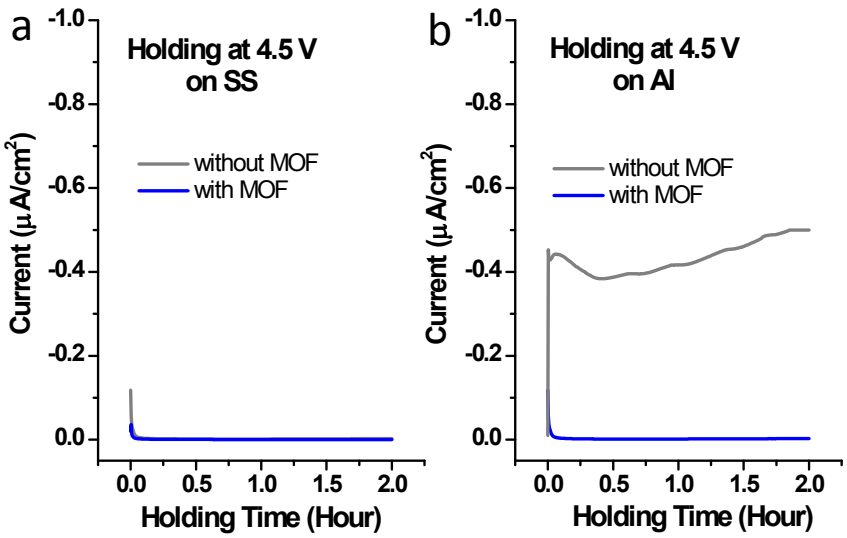

Figure S10. Voltage floating test for assessing the stability of current collectors (stainless steel/SS and aluminum/Al) towards TFSI anion in different condition: with (solvent-depleted electrolyte) and without MOF (typical electrolyte).

As can be found, compared with typical electrolyte, the solvent-depleted electrolyte can effectively suppress the corrosion of Al current collector under high voltage of 4.5 V.

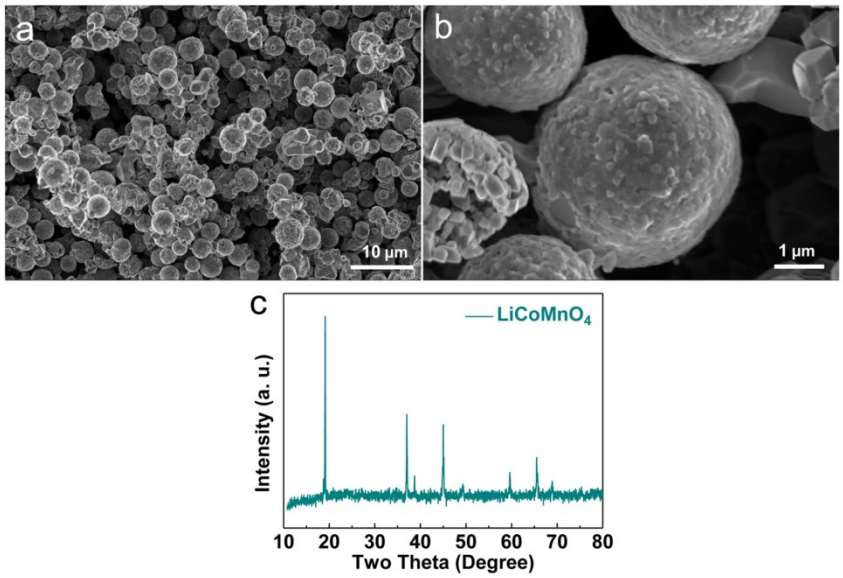

Figure S11. SEM images and XRD pattern of the prepared 5.3 V-class LCMO cathode material.

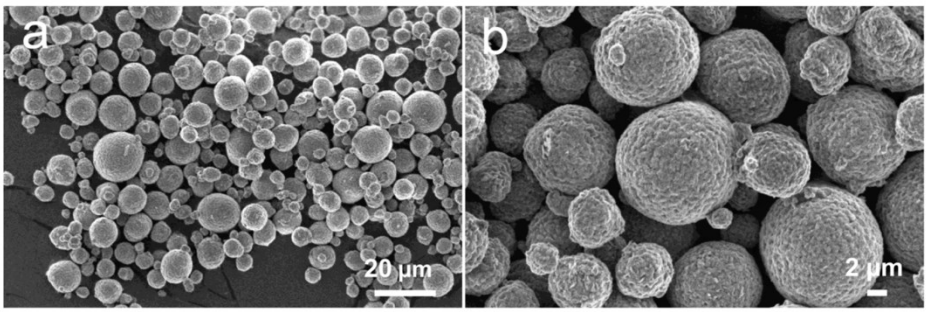

Figure S12. SEM images of the pristine NCM-811 particles.

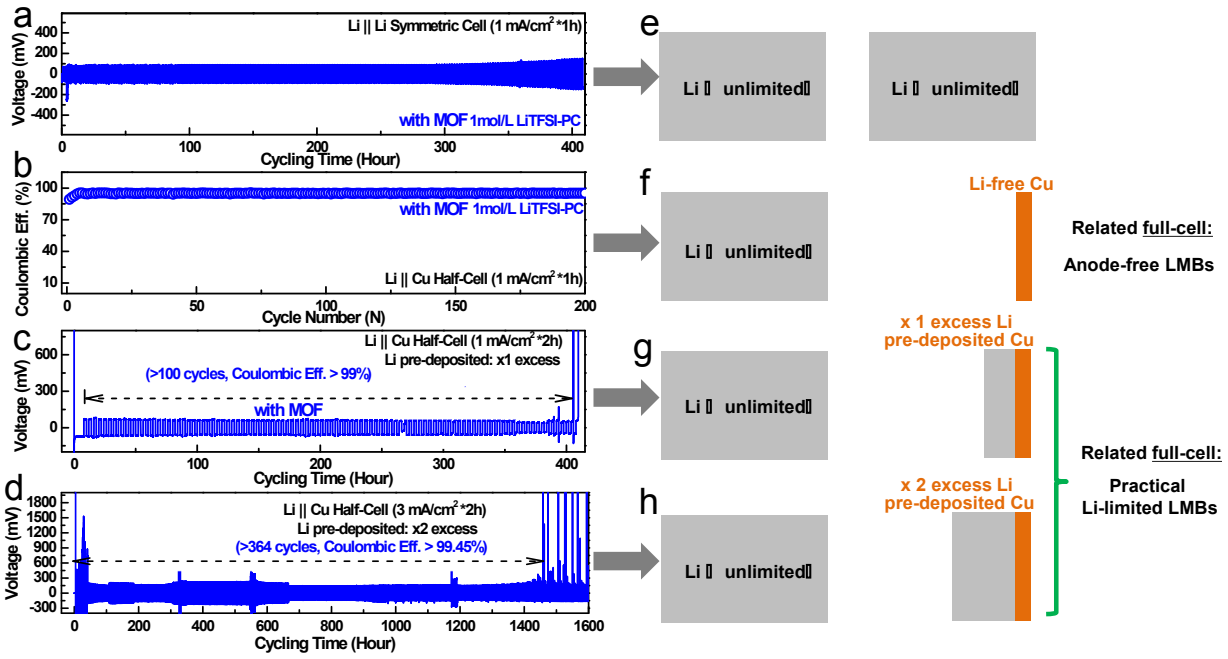

Figure S13. Symmetrical cell performances of the Li//Li and Li//Cu under different situations and the corresponding schematic diagram of cycling Li//Li and Li//Cu cells for measurement of Li coulombic efficiency.

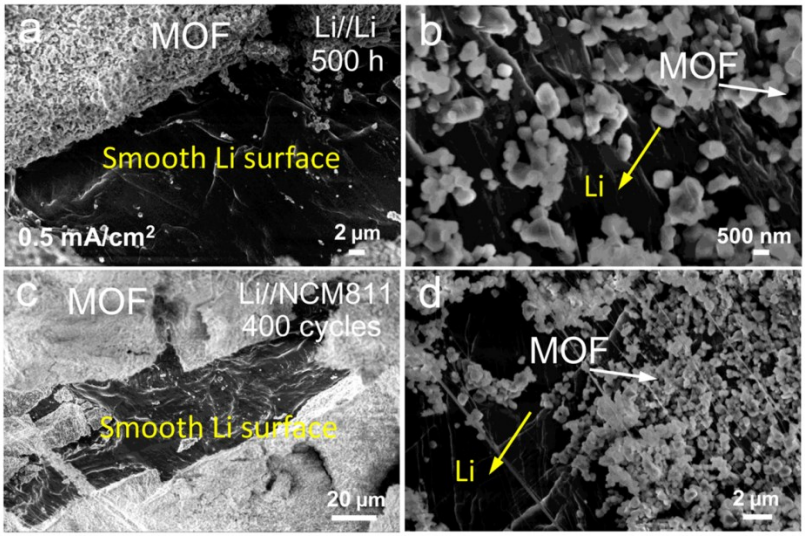

Figure S14. SEM of the cycled Li from the Li//Li cells using solvent-depleted electrolyte (PC-LiTFSI with MOF).

Li anodes harvested from the cycled cells (Li//Li after 500 hours and NCM811//Li cell after 400 cycles) both demonstrate smooth surface and without dendritic Li can be observed. MOF particles can also be found on the surface of cycled Li anodes.

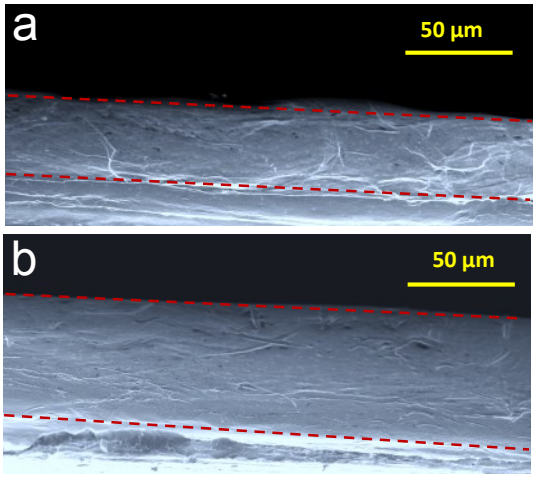

Figure S15. SEM images of the thin Li metals (a) 37.2 µm and (b) 66.0 µm.

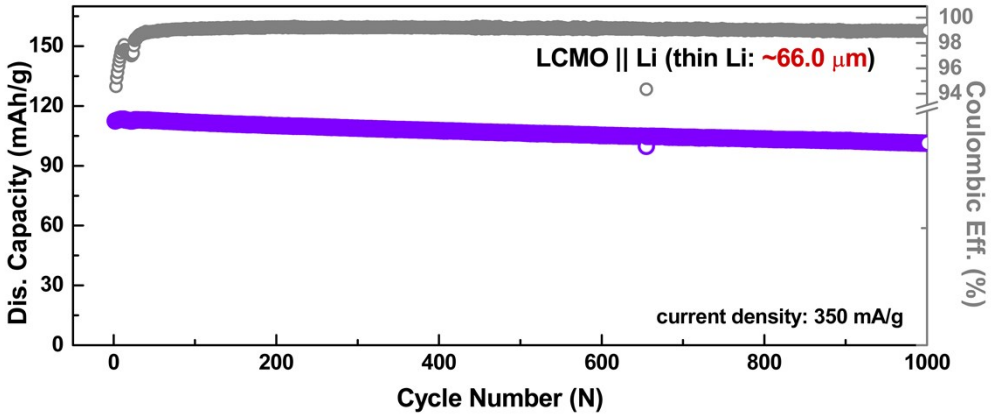

Figure S16. Discharge capacity against cycle number collected from LCMO//Li-metal cell using the solvent-depleted electrolyte under high LCMO cathode loading and thin Li about 66.0 μm.

Table S1. Parameter comparisons of all the cells tested in this work.

	NCM-811//Li Figure 7c	LCMO//Li Figure 7d	NCM-811//Li Figure 7e	LCMO//Li Figure 7f	LCMO//Li Figure S16	Li//Cu Cell (Figure 6)	
Current Density (mA/cm^2)	1.38	1.38	2.76	2.835	6.60	1.0	3.0
Capacity (mAh/cm^2)	1.564	1.288	3.306	2.835	2.08	2.0	6.0
Li excess	x 100%	x 100%	x 252%	x 289%	x 652%	x 100%	x 200%
Cycle Number	>150	>150	>400	~400	>1000	>100	>360

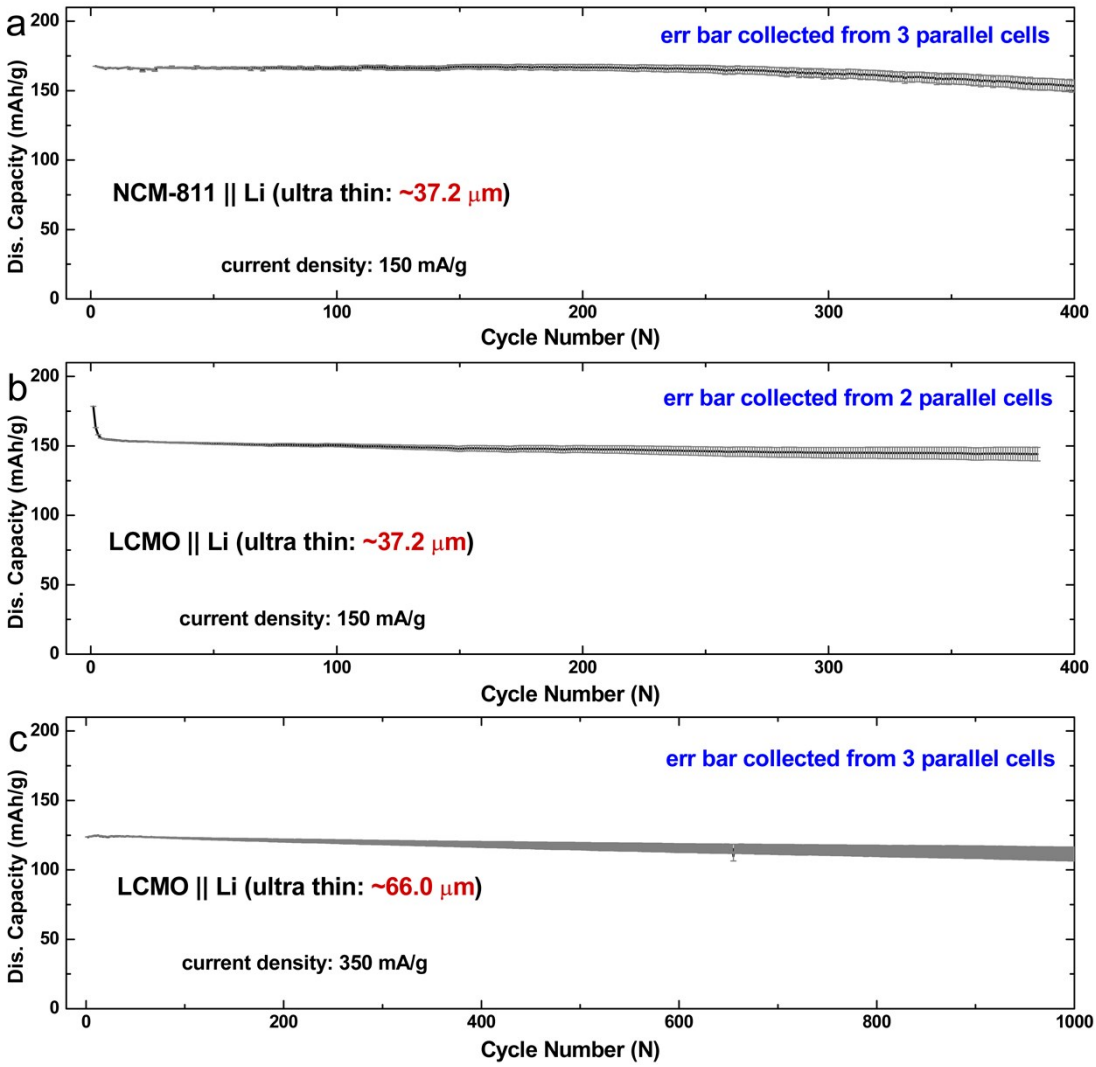

Figure S17. Electrochemical performances of parallel cells of cells tested in Figure 7 with error bar.

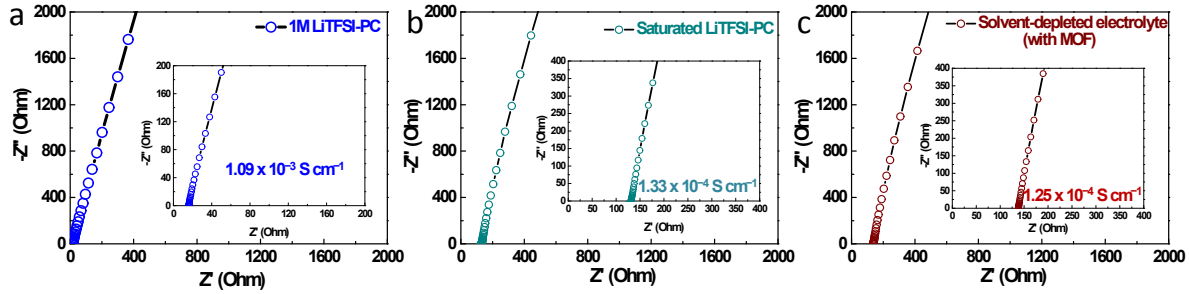

Figure S18. Electrochemical impedance spectra of the (a) diluent (1M) and (b) saturated LiTFSI-PC electrolyte and (c) the "solvent-depleted electrolyte".

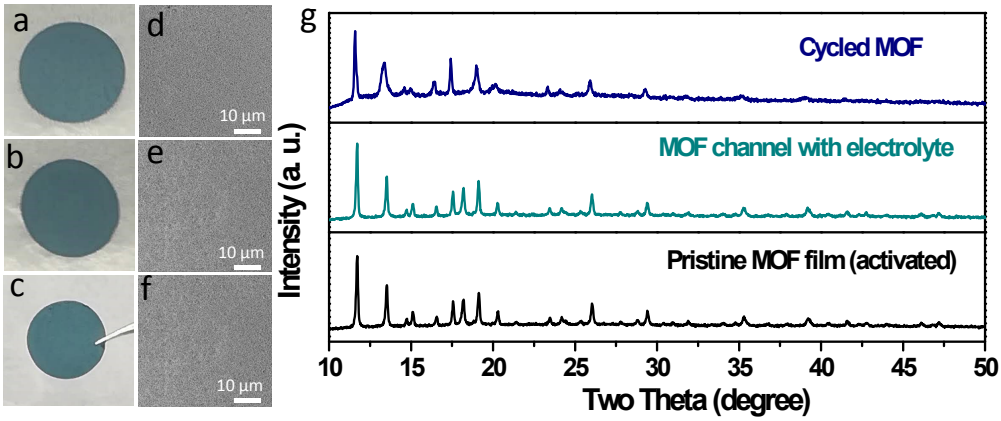

Figure R19. Stability of the prepared MOF film. (a-c) Digital photos of the MOF films. (a) Pristine MOF film, (b) MOF with electrolyte inside channels after vacuum treatment, (c) Cycled MOF film. (d-f) And the corresponding SEM images of the different MOF films. (g) XRD patterns of the cycled MOF film.

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