Electronic Supplementary Information

Modulating SEI Formation *via* Tuning Solvation Sheath for Lithium Metal Batteries

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Experimental section

Preparation of water-containing electrolyte For ether-based electrolytes preparation, LiTFSI (99.5% trace metals basis) and DEGDME (anhydrous, 99.5%) was purchased from Sigma-Aldrich. 1M LiTFSI in DEGDME solution were prepared inside an Ar-filled glovebox and stirred overnight. 1.3M $LiPF_6$ in EC/DEC = 3/7 (v/v) (PANAX, StarLyte, Korea) was used as a carbonate-based electrolyte. Standard water containing DEGDME solution was prepared as 25 wt% of deionized water in the DEGDME solvent. Before addition of DIW, the electrolytes are aged with molecular sieves overnight. To prepare 1,000, 10,000, and 20,000 ppm of deionized water electrolytes, the appropriate amount of standard solution is dropped by the micro-pipet (120, 1200, and 2400 μL of the standard solution, respectively) in the 30 g of LiTFSI in DEGDME electrolyte. In the case of 100,000 ppm of deionized water, 3 g of deionized water is added in 27 g of LiTFSI in DEGDME electrolyte. In the case of carbonate electrolyte, the process of adding water is the same as the ether electrolyte. All the samples were stored in a glass vial under argon inside the glovebox.

Physicochemical characterization of electrolytes To investigate changes in the chemical composition of fabricated electrolytes, Fourier-transform infrared spectroscopy (FT-IR, NICOLET 5700) was carried out. For FT-IR analysis, 0.2 g of pellets using KBr were made and the prepared electrolytes were dropped into the individual pellet. The viscosities of the prepared electrolytes were measured by a double gap viscometer system (Physica MCR 501) in room temperature. In the case of Li nucleation morphology analysis, to observe a more specific and detailed surface morphology of the Li deposit, a relatively low current density of 0.1 mA cm^{-2} for 0.1 mAh cm^{-2} was applied on a Cu substrate. And then, field-emission scanning electron microscopy (FE-SEM, JSM07600F) was used. X-ray photoelectron spectrometry (XPS, K-alpha plus (Thermo)) with an Al Ka X-ray source (1486.6eV) was used for analyzing

the changes in the SEI layer of the Li metal anode after 1 cycle including formation cycles according to electrolytes.

Electrochemical measurements 2032R coin type cell was used to evaluate the electrochemical test. To prepare $LiFePO_4$ (LFP) cathode, LFP, PVDF binder, and conducting agent (Ketjen black) in a weight ratio of 80:10:10 slurry in N-Methyl-2-pyrrolidone (NMP) was prepared. The slurry is casted on aluminum foils, followed by vacuum drying at 120 ^{o}C for 5 hours. The areal capacity of LFP electrode was 2 mAh cm^{-2} (11.75 mg cm^{-2} of mass loading). The lithium foils with a thickness of ~200 μm for symmetric cell and 20 μm for LFP full cell are used as lithium metal anodes. 2032R coin cell components were purchased from Wellcos Corporation, Korea. Before evaluation, all the cell components were dried at 110°C for 4h in a vacuum oven. 50 μL electrolyte was infused into each cell. Polypropylene (PP) separator was employed in cell fabrication. Fabricated coin cells were tested using a battery cycle tester (TOSCAT 3000, Toyo system, Tokyo, Japan). Linear sweep voltammetry (LSV) was performed in Autolab potentiostat / galvanostat (Model PGSTAT-72637) workstation using three-electrode configuration at ambient temperature. As the working electrode and counter electrode, a platinum disc electrode (1 cm^2) was used, and Ag/AgCl (KCL saturated) as the reference electrode was employed. For investigation of the electrochemical stability window for ether electrolytes with water, LSV was conducted between -3.25 V and 1.25 V versus Ag/AgCl at a scan rate of 10 mVs^{-1}.

Calculation on average Coulombic efficiency of Li anode for Li || LFP full cell The average Coulombic efficiency (C.E) is calculated based on the total cycle number (n) and loaded Li capacity. The theoretical gravimetric specific capacity (Cgrv) of Li metal is 3860 mAh g-1. The density (ρ) of Li metal is 0.534 g cm^{-3}. So, the capacity of 20 μm thick Li metal is calculated by below equation.

$C_{vol} = C_{grv} \cdot \rho$

$= 3860 \ (\text{mAh g}^{-1}) \cdot 0.534 \ (\text{g cm}^{-3})$

$= 2061.24 \ \text{mAh cm}^{-3}$

$C_{Li} = C_{vol} \cdot$ thickness of the Li

$= 2061.24 \ (\text{mAh cm}^{-3}) * 0.002 \ (\text{cm})$

$= 4.1 \ \text{mAh cm}^{-2}$

And the average capacity loss (C_{loss}) is calculated by below equations

$C_{loss} = C_{Li} / n$ (where n is cycle number for stable cycling with almost up to 99% coulombic efficiency in Fig. 3d)

C_{loss}, LFP||E-bare $= 4.1 \ \text{mAh cm}^{-2} / 8 = 0.513 \ \text{mAh cm}^{-2}$

The average capacity loss during one cycle implies irreversible capacity in the Li plating/stripping process for an average of one cycle. The average plating and stripping capacity of Li is the average cell capacity during stable cycle. For the Li || LFP cell in Fig. 3, the average areal cell capacity is C_{LFP}, avg $= 2 \ \text{mAh cm}^{-2}$. Subsequently, the average C.E of Li metal for Li || LFP full cell is calculated by the equation
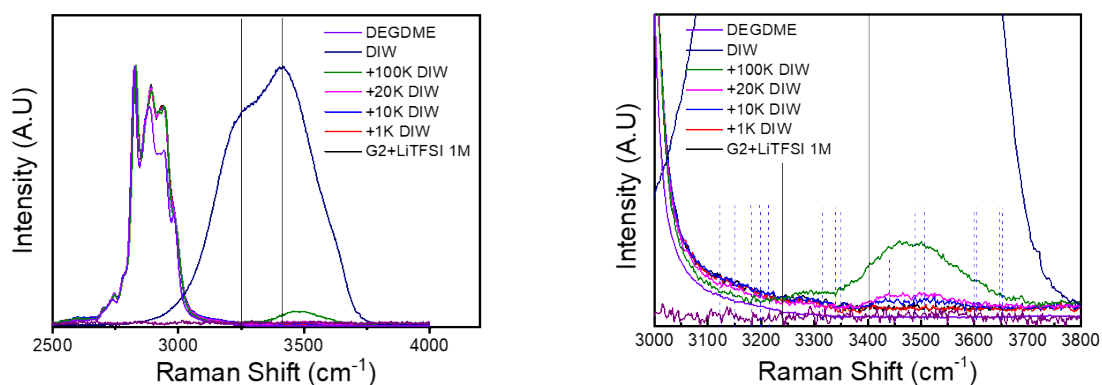
C.E (Li paired with cathode) = {areal capacity of cathode electrode – (C_{Li} / n) } / areal capacity of cathode electrode

C.E (E-bare) = { $2 \ \text{mAh cm}^{-2}$ - ($4.1 \ \text{mAh cm}^{-2} / 8$) } / $2 \ \text{mAh cm}^{-2}$

$= 74.4 \ \%$

C.E (E-DIW 1K) = { $2 \ \text{mAh cm}^{-2}$ – ($4.1 \ \text{mAh cm}^{-2} / 16$) } / $2 \ \text{mAh cm}^{-2}$

$= 87.2 \ \%$

C.E (E-DIW 10K) = { $2 \ \text{mAh cm}^{-2}$ – ($4.1 \ \text{mAh cm}^{-2} / 43$) } / $2 \ \text{mAh cm}^{-2}$

$= 95.3 \ \%$

Supplementary figures

H2O cluster peak position[1]	
Assignment	Peak position (cm^{-1})
Isolated H$_2$O	3153, 3657
Dimer	3602, 3606, 3651
Trimer	3121, 3438, 3491, 3506, 3711
Tetramer	3121, 3334, 3347, 3438, 3506
Pentamer	3121, 3310, 3506

Figure S1. Raman spectrum in the region of the OH stretching of the DEGDME, LiTFSI, DEGMDE(G2)+LiTFSI 1M electrolyte and addition of DIW samples.
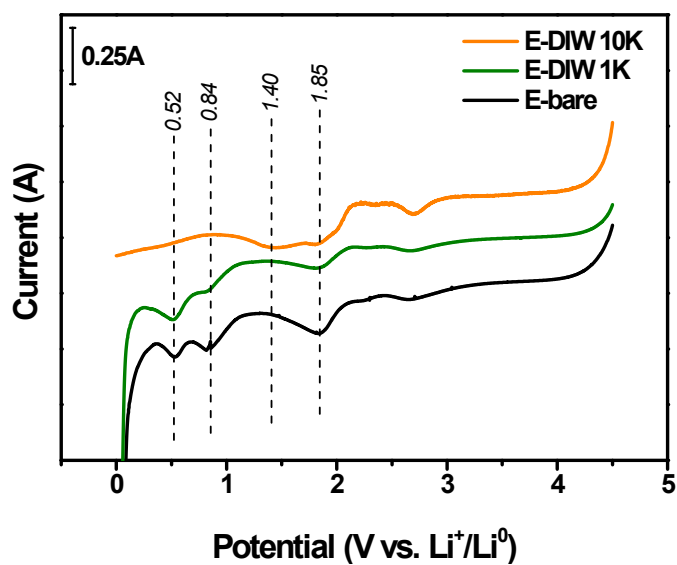
Figure S2. Linear sweep voltammetry (LSV) curves of prepared ether-based electrolytes.
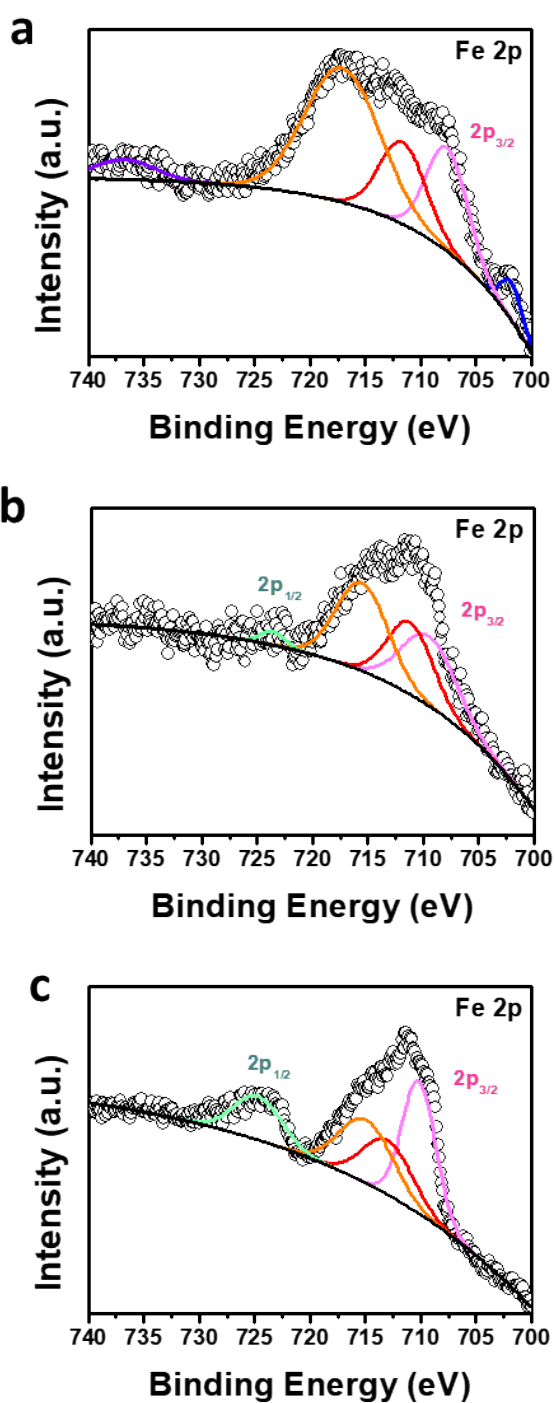
Figure S3. XPS analysis of the LFP cathode surface in the LFP||Li coin cells after 1cycle at 1C including formation cycles (1 cycle at 0.1C and 0.5C each) : Fe 2p XPS spectra of LFP cathode surface using (a) E-bare, (b) E-DIW 1K and (c) E-DIW 10K.
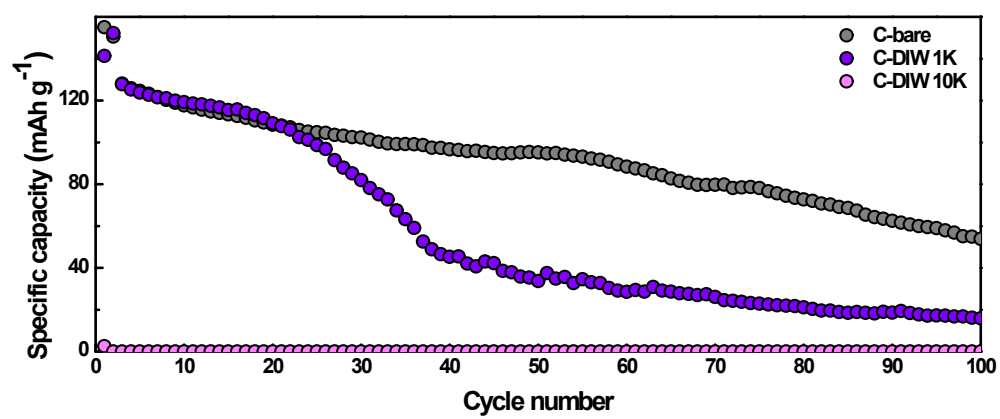
Figure S4. Cycling performance of LFP full cell using carbonate-based electrolyte with various water contents.
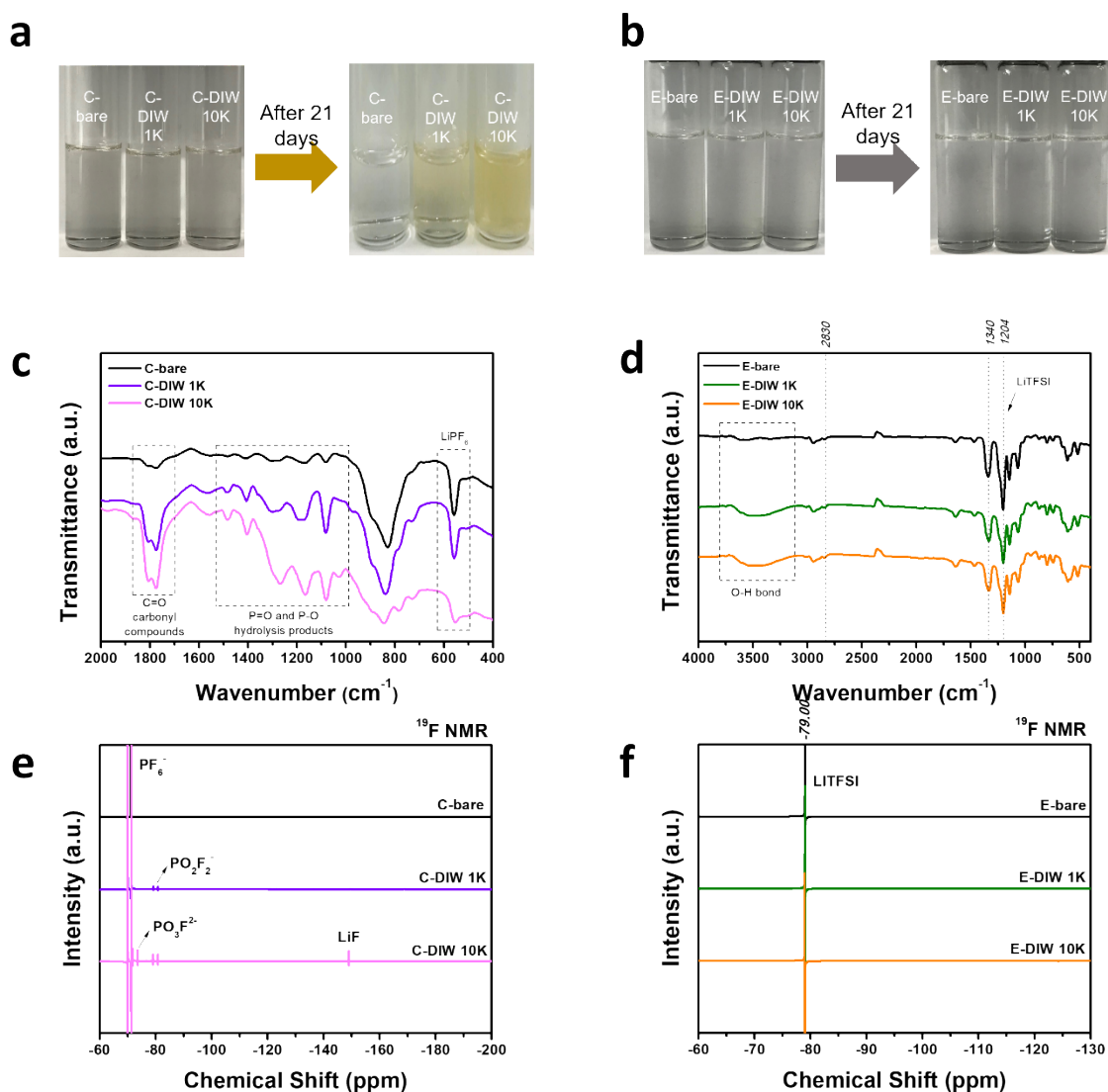
Figure S5. Comparison of the chemical stability in the water-containing condition between LiPF$_6$ 1.3 M in EC/DEC 3:7 (v/v) (C-bare) and LiTFSI 1M in DEGDME (E-bare) *via* addition of water (1,000 ppm; C-DIW 1K, E-DIW 1K and 10,000 ppm; C-DIW 10k, E-DIW 10K) electrolytes. (a-b) Optical images before and after aging for 21 days. (a) The optical images of LiPF$_6$ in EC/DEC 3:7 (b) Those of LiTFSI in DEGDME. (c-d) FT-IR analysis of both electrolytes after 21 days. (c) FT-IR analysis results of carbonate electrolytes (d) FT-IR analysis results ether electrolytes. (e-f) ^{19}F NMR spectra of carbonate(e) and ether(f) electrolytes after 21 days from the addition of DIW according to water concentration.