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Supporting Information

A universal strategy for high-voltage aqueous batteries via lone pair electrons as hydrogen bond-breaker

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The PDF file mainly contains the following: Figure S1-S17, Table S1-S6, Refs. 1-21.

Experimental Section

Preparation of "LiTFSI(TMS)_m**Water**_n" **electrolyte:** Lithium bis (trifluoromethane sulfonyl) imide (LiN(SO₂CF₃)₂, LiTFSI) (>98%) was purchased from TCI. Tetramethylene sulfone (TMS) and HPLC–grade water were purchased from Sigma–Aldrich. LiNi_{0.5}Mn_{1.5}O₄ and Li₄Ti₅O₁₂ materials were provided from MTI Corporation, USA. The aqueous "LiTFSI(TMS)_mWater_n" electrolyte was prepared by by mixing LiTFSI with TMS and water at a series of molar ratios (LiTFSI/TMS/H₂O,1:1:1, 1:0.5:1, 1:0.5:1.8). The LiTFSI/TMS solution was prepared in an argon-filled glove box to prevent air pollution. Then water was added in the proportion and stirred sufficiently for 12h. For convenience, we named the three hydrated "LiTFSI(TMS)_m(Water)_n" electrolytes with different molar ratios as "LiTW, LiT_{0.5}W, LiT_{0.5}W_{1.8}".

Electrode fabrication: To prepare the $LiNi_{0.5}Mn_{1.5}O_4$ films and $Li_4Ti_5O_{12}$ films, the active materials were mixed with carbon black (Shenzhen Chuangyu) and polyvinylidene fluoride binder (PVDF, Shanghai Songjing) in dispersing agent N-methyl-2-pyrrolidone (NMP) at a weight ratio of active materials: carbon black: PVDF=8:1:1 onto the Ti foil and an Al foil, respectively. The obtained slurries were dried at 80 °C under vacuum for 12 h. Then they were punched out into 1 cm² disc electrodes with a mass loading of about 2.7 mg cm⁻² for LiNi_{0.5}Mn_{1.5}O₄ electrode and

1.3 mg cm⁻² for Li₄Ti₅O₁₂ electrode.

Materials Characterizations: FTIR spectroscopy were performed using Nicolet 6700 FTIR spectrometer between 4000 and 100 cm⁻¹. Raman spectra and in-situ Raman spectra patterns at room temperature were performed using Bruker RFS100/S and Thermo DXR2 Raman microscope with a 532 nm diode-pumped solid-state laser between 3500 and 100 cm⁻¹. Variable temperature Raman spectroscopy were performed using LABRAM HR EVOLUTION JR between 4000 and 100 cm⁻¹. The thermal imaging technique were tested using infrared American FLIR T540. The CEI and SEI morphology images were tested using Transmission electron microscopy (TEM) images of FEI Tecnai G2 F20 X-TWIN transmission electron microscope. The samples were disassembled from the cycled coin full cell and cleaned by DME for three times to remove residual lithium salts. Then dissolving the electrodes in DME solution and ultrasonic disperse for 30 minutes. The DEMS test was performed on a commercial mass spectrometer (Hiden, Beijing) that was combined with the assembled Swagelok cells containing LiNi_{0.5}Mn_{1.5}O₄, Li₄Ti₅O₁₂, glass fiber separator, a piece of Ti foil, Al foil, stainless spacer (1 mm in height), and 150 µL electrolytes. Before testing, the airtight Swagelok cells was ventilated with ultrahigh pure Ar for 2 hours to remove impurity gas. The continuous pure Ar gas ($\sim 5 \times 10^6$ Torr) was then allowed to in situ monitor the gas released from the inner space of cell and subsequently analyzed in the mass spectrometer.^[1] XPS measurements (PHI-1600, USA) were conducted to characterize the chemical composition of electrodes surface with monochromatic Al-Ka (1486.6 eV) radiation.

Electrochemical Measurements: The ionic conductivity was determined using a.c. impedance spectroscopy with a ZAHNER Electrochemical Workstation. The electrochemical stability window was measured by CV (CHI 660E Electrochemical Analytical Instrument (Chenhua)) using three-electrode system containing Pt electrode (anodic limit) and Al electrode (cathodic limit) working electrode, activated carbon counter electrode, and Ag/AgCl (in saturated KCl aqueous solution) reference electrode at a scan rate of 5 mV·s⁻¹. The CV testing of LiNi_{0.5}Mn_{1.5}O₄ and Li₄Ti₅O₁₂ reversibility reactions were performed using three-electrode system consisting of LiNi_{0.5}Mn_{1.5}O₄ and Li₄Ti₅O₁₂ working electrodes, activated carbon counter electrode and Ag/AgCl reference electrodes at the scan rate of 0.5 mV·s⁻¹. he potential should be converted into the standard Li⁺/Li, supposing that the potential of Ag/AgCl electrode is 3.239 V vs. Li⁺/Li. The galvanostatic charge-discharge test tests were performed on a LAND-CT2001A battery test system (Wuhan, China) at different rates between 2.0-3.5 V. The loading of LiNi_{0.5}Mn_{1.5}O₄ and Li₄Ti₅O₁₂ were 2.73 mg/cm² and 1.29 mg/cm² respectively. The mass ratio of LiNi_{0.5}Mn_{1.5}O₄- Li₄Ti₅O₁₂ was about 2:1, aiming to compensate for the irreversible capacity caused by the formation of SEI in the first few cycles. In order to eliminate side reactions, the φ 18 mm Ti foil and φ 16 mm Al foil were placed between the positive electrode/ negative electrode sheet and the stainless steel shell.

Calculation of energy density of the full cell: The energy density of full cell at 25 °C and -60 °C was calculated based on the first discharge capacity at 6 C and 0.1 C rate

respectively and the sum loading mass of cathode and anode active materials.^[2] The calculations are based on Eq. 1:

Specific energy
$$(Wh \cdot kg^{-1}) = \frac{discharge \ capacity \times operating \ voltage}{the \ total \ loading}$$
(1)

Specific energy
$$(Wh \cdot kg^{-1})_{25 \circ C} = \frac{0.174 \times 10^{-3} Ah \times 3.15 V}{4.02 \times 10^{-6} kg} \approx 136 Wh \cdot kg^{-1}$$

Specific energy
$$(Wh \cdot kg^{-1})_{-60^{\circ}C} = \frac{0.0316 \times 10^{-3} Ah \times 3.15 V}{3.97 \times 10^{-6} kg} \approx 25 Wh \cdot kg^{-1}$$

MD Simulation details: To represent the LiTFSI-H₂O-TMS electrolyte, a model system consisted of 1000 LiTFSI, 1000 water, and 450 TMS molecules was built. At the beginning of the simulation, energy of the model system was minimized. After that, two NPT molecular dynamics simulations of 1000 ps at two temperatures (193.15 K, 298.15 K and 333.15 K) and pressure (1 atm) were performed, which brought the system into a reasonable preequilibrated configuration for subsequent simulations. After that, a further 1000 ps NVT ensemble molecular dynamics simulation was conducted at 193.15 K, 298.15 K and 333.15 K to track changes in the system.

In this work, Packmol ^[3] was used to build initial configuration of the model system. LAMMPS ^[4] and PCFF-INTERFACE force field ^[5] were used to perform the molecular simulations. The time step was fixed at 1.0 fs, and the temperature and pressure were controlled by the Nosé-Hoover thermostat-barostat ^[6]. A van der Waals interaction cutoff of 1.5 nm was employed, and the PPPM method was used to account for the long-range electrostatic interactions ^[7]. The atomic coordinates were saved every 1 ps for post-analysis.

Figures



Figure S1. The optical photographs of electrolytes at different temperatures of 25, 10, 0, -10, -20, -30, -40, -50, -60 °C (They are $LiT_{0.5}W_{1.8}$, LiTW, $LiT_{0.5}W$, LiTFSI/TMS, TMS/H₂O, TMS, H₂O from left to right)



Figure S2. Real-time temperature monitoring diagram from infrared thermal imaging after mixing TMS with H_2O .



Figure S3. The model system of $LiT_{0.5}W$ electrolyte consisted of 1000 LiTFSI, 1000 water, and 450 TMS molecules. Colors: Li^+ , purple; O, red; C, grey; H, white; N, blue; S, yellow; F, cyan.



Figure S4. The Li–O and Li-N coordination numbers of LiT $_{0.5}$ W electrolyte at 333.15 K.



Figure S5. The Li–O and Li-N coordination numbers of $LiT_{0.5}W$ electrolyte at 193.15 K.



Figure S6. Total numbers of hydrogen bonding formed from $1TMS-1H_2O$ and $1TMS-2H_2O$ in LiT_{0.5}W electrolyte at 333.15 K.



Figure S7. Total numbers of hydrogen bonding formed from $1TMS-1H_2O$ and $1TMS-2H_2O$ in $LiT_{0.5}W$ electrolyte at 193.15 K.



Figure S8. The snapshots of hydrated shell coordination compounds Li(TFSI)_m(H₂O)_n.



Figure S9. The mean-squared displacement (MSD) of different species calculated for $LiT_{0.5}W$ electrolyte.



Figure S10. Cyclic voltammograms of the $LiNi_{0.5}Mn_{1.5}O_4$ - $Li_4Ti_5O_{12}$ full cell with a scan rate of 5 mV/s and 10 mV/s using $LiT_{0.5}W$ as the electrolyte.



Figure S11. The TEM images of a) pristine Li₄Ti₅O₁₂ b) cycled Li₄Ti₅O₁₂ in LiTW electrolyte.



Figure S12. The TEM images of a) pristine LiNi_{0.5}Mn_{1.5}O₄ b) cycled LiNi_{0.5}Mn_{1.5}O₄ in LiTW electrolyte c) cycled LiNi_{0.5}Mn_{1.5}O₄ in LiT_{0.5}W electrolyte.



Figure S13. Voltage profiles of $LiNi_{0.5}Mn_{1.5}O_4$ - $Li_4Ti_5O_{12}$ full cell using $LiT_{0.5}W_{1.8}$ electrolyte after the first cycle corresponding to the DEMS.



Figure S14. Voltage profiles of LiNi_{0.5}Mn_{1.5}O₄-Li₄Ti₅O₁₂ full cell using LiTW electrolyte after the first cycle corresponding to the DEMS.



Figure S15. Voltage profiles of $LiNi_{0.5}Mn_{1.5}O_4$ - $Li_4Ti_5O_{12}$ full cell using $LiT_{0.5}W$ electrolyte after the first cycle corresponding to the DEMS.



Figure S16. The cycle performance of repeated $LiNi_{0.5}Mn_{1.5}O_4/Li_4Ti_5O_{12}$ full cell with $LiT_{0.5}W$ electrolytes at 6 C at 25 °C.



Figure S17. Schematic representation of the in-situ cell for in-situ Raman experiment.

Sovlent	Name	Structure	melting point (°C)	boiling point(°C)	DN value (kcal·mol ⁻¹)
DMSO	Dimethyl sulfoxide		18.45	189	29.8 ^[8]
MSM	Methyl sulfone	0 	107	238	15 ^[9]
TMS	Tetrameth ylene sulfone	o o s	28.4	287.3	14.8 ^[10]
EMS	Ethyl Methyl Sulfone	0 S	34	239.2	13[9]
EiPS	Ethyl Isopropyl Sulfone	0 S	-9.1	91	15 ^[9]
MSL	3- Methylsulf olane		0.5	104	15 ^[9]

 Table S1. Summary of the chemical structure, physical characteristics and abbreviation of typical sulfone solvents.

conductivities/mS·cm ⁻¹				
temperature/°C	LiT _{0.5} W _{1.8}	LiTW	LiT _{0.5} W	
-80	2.17×10-4	1.32×10 ⁻⁴	1.03×10 ⁻⁴	
-70	4.48×10 ⁻⁴	2.23×10 ⁻⁴	2.28×10 ⁻⁴	
-60	6.81×10 ⁻⁴	2.23×10 ⁻⁴	1.47×10 ⁻⁴	
-50	2.68×10-3	1.20×10 ⁻³	4.14×10 ⁻⁴	
-40	2.49×10-2	2.69×10-3	4.64×10-4	
-30	5.27×10-2	9.05×10-3	1.87×10-3	
-20	1.47×10 ⁻¹	3.27×10 ⁻²	6.44×10 ⁻³	
-10	3.23×10 ⁻¹	8.71×10 ⁻²	2.30×10 ⁻²	
0	6.19×10 ⁻¹	1.84×10 ⁻¹	5.92×10 ⁻²	
10	1.12	3.55×10 ⁻¹	1.28×10 ⁻¹	
20	1.78	6.44×10 ⁻¹	2.52×10 ⁻¹	
25	2.38	8.87×10 ⁻¹	3.71×10 ⁻¹	
30	3.24	1.09	4.10×10 ⁻¹	
40	4.01	1.60	6.63×10 ⁻¹	
50	5.65	2.35	1.06	
60	7.20	3.21	1.56	
70	9.30	4.54	2.23	
80	11.50	5.88	3.03	
90	13.90	7.34	4.07	
100	16.80	8.86	5.17	

Table S2. Ionic conductivities of $LiT_{0.5}W_{1.8}$, LiTW and $LiT_{0.5}W$ electrolytes at different temperatures of -80~100 °C.

Table S3. Ionic conductivities of different aqueous electrolytes at low temperatures.^[11]

conductivities/mS·cm ⁻¹				
temperature/°C	-80	-60	-40	
LiT _{0.5} W _{1.8}	2.17×10-4	6.18×10 ⁻⁴	2.49×10 ⁻²	
LiTW	1.32×10 ⁻⁴	2.23×10-4	2.69×10 ⁻³	
LiT _{0.5} W	1.03×10 ⁻⁴	1.47×10 ⁻⁴	4.64×10 ⁻⁴	
2m ZnSO ₄	-	2.52×10 ⁻¹¹	6.41×10 ⁻⁹	
2m Zn(CF ₃ SO ₃) ₂	-	3.79×10 ⁻⁸	9.19×10 ⁻¹	

Percentage (%)					
193.15 K 298.15K 333.15 K					
$H_2O_{1TMS-1H_2O}$	13.97	11.01	11.16		
$\mathrm{H_2O_{1TMS-2H_2O}}$	2.20	1.32	1.13		
Other H ₂ O	83.83	87.67	87.71		

Table S4. Percentage of water in different forms calculated for $LiT_{0.5}W$ electrolyte.

Table S5. Diffusion coefficient of different species calculated for $LiT_{0.5}W$ electrolyte.

Diffusion coefficient (10 ⁻⁷ cm ² /s)					
193.15 K 298.15K 333.15 K					
TMS	0.322	3.24	4.47		
TFSI	0.000404	0.395	0.274		
Li	0.00102	0.332	0.226		
H_2O	25.405	370.33	463.6		

Table S6. The key principle and performance comparison of our work with the representative aqueous batteries.

Refer ences	Cathode anode	Electrolyte/ Electrochemical window	Performance	Principle
this work	LiNi _{0.5} Mn _{1.5} O ₄ Li ₄ Ti ₅ O ₁₂	LiTFSI-H ₂ O- TMS 5.4V	126 mAh/g _{anode} , 10 C,300cycles, 136 Wh·kg ⁻¹	Introducing the "hydrogen bond-captured" solvent TMS to achieve the aqueous ESW of 5.4 V and huge temperature range of - 80~60 °C
Ref. [12]	LiMn ₂ O ₄ Mo ₆ S ₈	LiTFSI-H ₂ O 3V	47 mAh/g _{total weight} , 0.15 C,100cycles, 84 Wh·kg ⁻¹	A highly concentrated"water-in-salt" electrolyte whose window was expanded to ~3.0 V with the formation of LiF-rich SEI

Ref. [13]	LiMn ₂ O ₄ L-TiO ₂	LiTFSI-H ₂ O- PAM 3.1 V	138 mAh/g _{anode} , 1C, 100 cycles	Introducing PAM into "water-in-salt" electrolyte as an additive that assists in the formation of a stable SEI
Ref. [14]	LiMn ₂ O ₄ Li ₄ Ti ₅ O ₁₂	LiTFSI-H ₂ O- PEG 3.2 V	50 mAh/g _{total weight} , 1 C, 300 cycles, 110 Wh·kg ⁻¹	Molecular crowding electrolytes using the water-miscible polymer PEG as the crowding agent
Ref. [15]	$LiMn_2O_4 \\ Li_4Ti_5O_{12}$	LiTFSI-H ₂ O- Me ₃ EtN·TFSI 3.25 V	56 mAh/g _{total weight} , 1C, 150 cycles, 145 Wh·kg ⁻¹	The 63m aqueous electrolyte was achieved by introducing non-Li cosalt Me ₃ EtN·TFSI to alter the Li ⁺ -solvation sheath structure
Ref. [16]	Li _{1.5} Mn ₂ O ₄ Li ₄ Ti ₅ O ₁₂	LiTFSI-H ₂ O- KOH– CO(NH ₂) ₂ 3.3 V	65 mAh/g _{total weight} , 1 C,470 cycles	Using CO(NH ₂) ₂ as a model diluent, the reduction of LiTFSI and CO(NH ₂) ₂ under KOH catalyst formed a robust LiF/polymer bilayer SEI
Ref. [17]	LiCoO ₂ Li ₄ Ti ₅ O ₁₂	LiTFSI-H ₂ O- LiBETI 3.8 V	53 mAh/g _{total weight} , 10C, 200 cycles, 130 Wh·kg ⁻¹	Developing a hydrate-melt electrolyte that all water participates in the Li^+ hydration shells while retaining their fluidity
Ref. [18]	LiNi _{0.5} Mn _{1.5} O ₄ Li ₄ Ti ₅ O ₁₂	LiTFSI-H ₂ O- DMC 4.1 V	160 mAh/g _{anode} , 6 C,1000cycles, 165 Wh·kg ⁻¹	Introducing the secondary interfacial ingredient DMC to regulate the inner-Helmholtz regions
Ref. [19]	LiMn ₂ O ₄ Li ₄ Ti ₅ O ₁₂	LiTFSI-H ₂ O- TEGDME 4.2 V	155 mAh/g _{anode} , 3 C, 500 cycles, 120 Wh·kg ⁻¹	Introducing the secondary co-solvent TEGDME to boost stable interfacial chemistry
Ref. [20]	AC NaTi ₂ (PO ₄) ₃	NaClO ₄ -H ₂ O- DMSO -	68 mAh/g _{anode} , 0.5 C, -50°C, 100 cycles	Forming stable H-bonds by combining DMSO and H_2O to achieve the electrolytes with a freezing point lower than -130 °C
Ref. [21]	$\begin{array}{c} LiMn_2O_4\\ Li_4Ti_5O_{12} \end{array}$	LiTFSI-H ₂ O- AN 4.5 V	161 mAh/g _{anode} , 1C, 300 cycles, 109 Wh∙kg ⁻¹	Introducing AN to generate a thin and uniform interphase consisting of C≡N, R- S-N-S and LiF species

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