Supporting Information

Water-in-Salt Electrolytes for Aqueous Lithium-Ion Batteries with Liquidus Temperatures Below −10 °C

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Experimental Section

LiPTFSI (≥98%, Provisco), LiOTf (99.995 %, Sigma-Aldrich), LiTFSI (99.9%, Solvionic), LiBETI (>99%, Iolitec), LiFSI (battery grade, Fluorochem), LiFTFSI (≥98%, Provisco) were used as received and stored under an inert argon atmosphere in a glovebox (MBraun). The electrolytes were prepared by dissolving one or two salts in high-purity water (deionized water further purified with a Millipore Milli-Q water purification system). Due to some acidic impurities, the pH values of the LiPTFSI-based electrolytes were adjusted to 6−7 using degassed lithium hydroxide solutions. pH values were determined using pH paper (Merck) with a detection range from 1 to 14.

Differential scanning calorimetry was carried out with a Netzsch STA 449 F3 simultaneous thermal analyzer. Ca. 30 mg of electrolyte sample were mixed with ca. 1 mg of meso-carbon microbeads as crystallization agent and hermetically sealed in Al pans. All measurements were carried out at a scan rate of 1 °C min^{-1}. The samples were equilibrated at 60 °C for 30 min prior to the start of the measurement.

Photographs of the samples sealed in NMR tubes were taken after storage for at least 12 h at −40 °C, −20 °C, −10 °C, 0 °C, 10 °C, and 25 °C, respectively. The temperature was controlled with a climatic chamber (Binder MK 53).

Ionic conductivity was determined via impedance spectroscopy (Bio-Logic MCS 10) in sealed 2-electrode cells equipped with Pt electrodes (Bio-Logic HTCC). Viscosity was determined with a Kyoto Electronics Manufacturing EMS-1000 electromagnetically spinning viscometer. Density was measured with an Anton Paar DMA 4100 M density meter.

Raman spectra of selected electrolytes sealed in NMR tubes were collected at room temperature on a Renishaw Ramascope using a laser with a wavelength of 633 nm.

Electrochemical stability windows were determined via linear sweep voltammetry in 3-electrode Swagelok cells with a Bio-Logic VMP3 electrochemical workstation. Gold-coated ($d = 100$ nm) stainless steel electrodes were used as working electrodes, activated carbon pellets were used as counter electrodes, and a miniature Ag/AgCl electrode (eDAQ) was used as reference electrode. Cathodic and anodic sweeps were carried out separately with freshly prepared cells. The scan rate was set to 1 mV s^{-1}.

$LiMn_2O_4$ electrodes with a diameter of 12 mm and an active material mass loading of 4.5 to 5.5 mg cm^{-2} were prepared from *N*-methyl-2-pyrrolidone (NMP)-based slurries on stainless steel current collectors. The composition of the electrodes was 80 wt% active material (D50: 17.5 µm, type: SLMO03001, Targray), 10 wt% polyvinylidene difluoride (PVdF) binder (Arkema Kynar HSV900), and 10 wt% carbon black (IMERYS Graphite & Carbon C-NERGY SUPER C65). The electrodes were pressed at 1 t cm^{-2} for 30 s. 3-electrode Swagelok cells containing a $LiMn_2O_4$ working electrode, an activated carbon pellet as counter electrode, a miniature Ag/AgCl reference electrode (eDAQ), Whatman glass fiber separators, and ca. 200 µL of electrolyte were assembled in ambient atmosphere. The cells were subjected to galvanostatic charge/discharge cycling at a rate of 1C using a Bio-Logic VMP3. 1C was defined as 148 mA g_{AM}^{-1}. The lower and upper cut-off potentials for the $LiMn_2O_4$ electrodes were set to 0.6 and 1.5 V vs. Ag/AgCl, respectively. Prior to the first cycle (after at least 2 h of thermal equilibration) and after every 20 cycles, the cell impedance was recorded in a frequency range of 200 kHz to 100 mHz with the amplitude set to 10 mV. The cycling experiments were conducted at room temperature (ca. 25 °C), 0 °C (in a Binder KB 115), and −10 °C (in a Binder MK 53).

Impedance spectroscopy

The relative cell resistances shown in Figure S5 were calculated by dividing the current cell resistance by the initial cell resistance (prior to cycling). The cell resistance was defined as the high-frequency intercept of the impedance curve with the real axis in a Nyquist plot. Figure S1 shows an exemplary Nyquist plot with the cell resistance as defined above marked with an arrow. We assign the reduction in cell resistance during cycling visible for some of the cells in Figure S5 to improved wetting, particularly of the pellet-type activated carbon counter electrode.

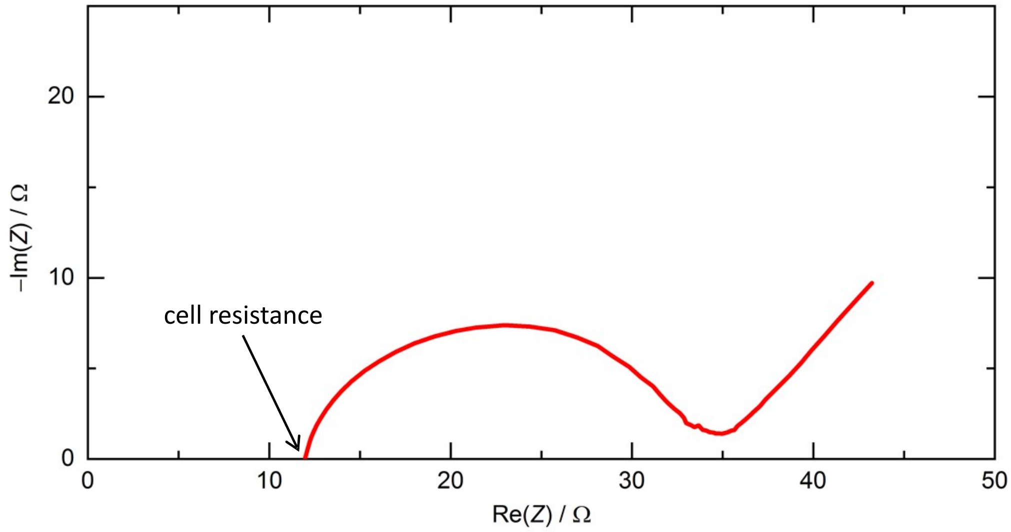

Figure S1: Nyquist plot of exemplary impedance data for a $LiMn_2O_4$/activated carbon half cell used in this study. The arrow illustrates how cell resistance is defined in this study.

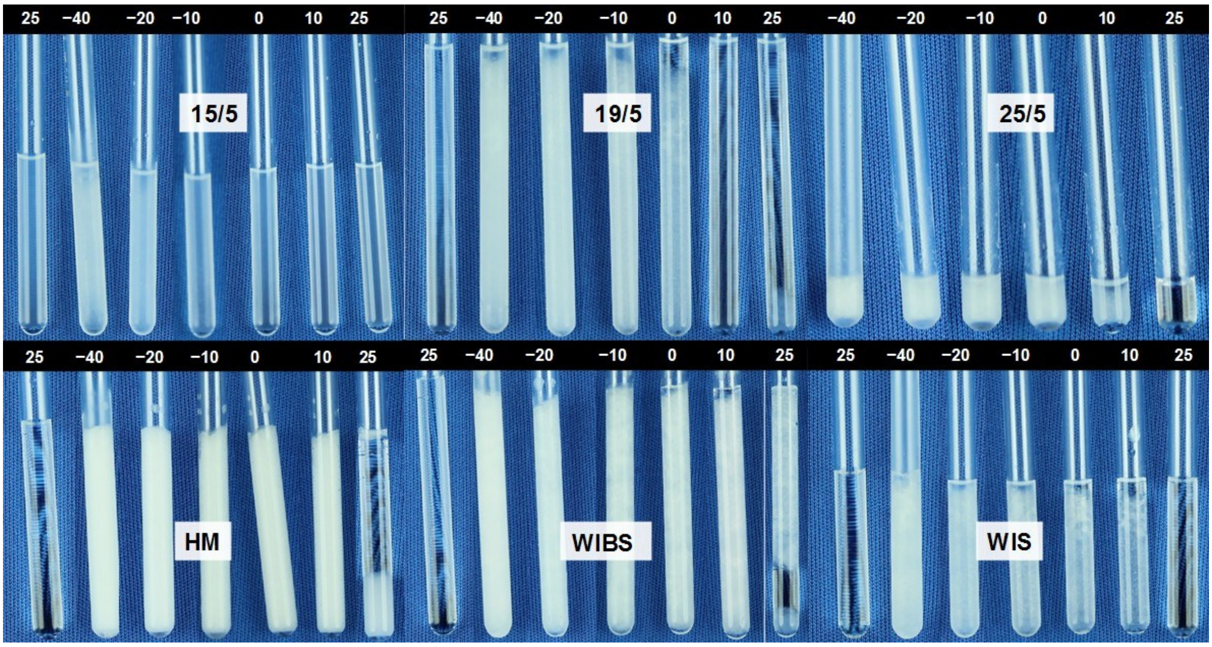

Figure S2: Photographs of selected electrolytes after storage at various temperatures for at least 12 h. The white number in the black bar above each NMR tube indicates the storage temperature at which the photograph was taken. Upper row: Electrolytes with different LiPTFSI:LiOTf ratios. Lower row: Hydrate-melt (HM), water-in-bisalt (WIBS), and water-in-salt (WIS) electrolytes for comparison.

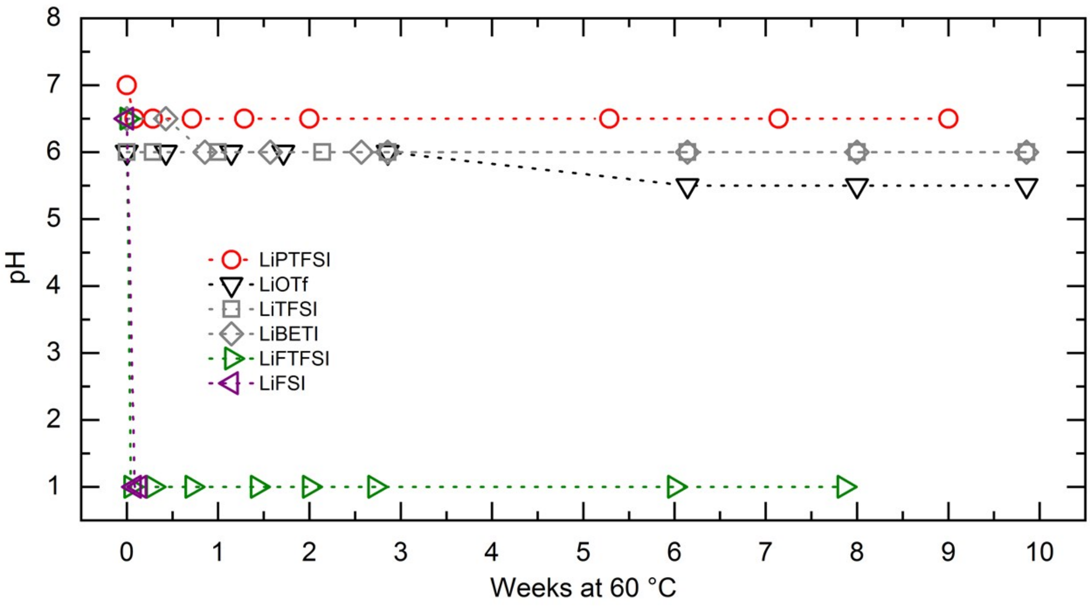

Figure S3: Chemical stability of common anions used for water-in-salt electrolytes. The figure shows the evolution of the pH of 20m aqueous solutions of LiOTf, LiFSI, LiFTFSI, LiTFSI, LiPTFSI, and LiBETI, respectively, during storage at 60 °C.

Table S1: Numerical data used to construct the Walden plot (Figure 2b). The table contains density (ρ), conductivity (σ), molar conductivity (Λ), and viscosity (η) data for selected electrolytes in a temperature range from 10 to 60 °C.

Electrolyte	T / °C	ρ / g cm^{-3}	σ / mS cm^{-1}	Λ / S cm^{2} mol^{-1}	η / Poise^{-1}
15/5	10	1.739	3.90	0.775	1.86
	20	1.727	5.70	1.14	1.10
	25	1.721	6.75	1.36	0.870
	30	1.715	7.88	1.59	0.709
	40	1.702	10.5	2.13	0.484
	50	1.690	13.6	2.78	0.339
	60	1.678	17.0	3.50	0.248
19/5	10	1.770	1.95	0.379	4.06
	20	1.757	2.98	0.584	2.28
	25	1.751	3.62	0.712	1.77
	30	1.744	4.33	0.855	1.41
	40	1.732	5.99	1.19	0.901
	50	1.720	7.91	1.58	0.616
	60	1.709	10.2	2.06	0.432
20/0	10	1.754	3.60	0.795	2.55
	20	1.741	5.31	1.18	1.45
	25	1.734	6.46	1.44	1.14
	30	1.728	7.62	1.71	0.898
	40	1.715	10.2	2.30	0.588
	50	1.703	13.3	3.01	0.402
	60	1.692	16.7	3.81	0.291
WIBS	10	1.770	1.91	0.317	4.64
	20	1.758	3.00	0.502	2.54
	25	1.752	3.69	0.619	1.94
	30	1.746	4.46	0.751	1.59
	40	1.734	6.25	1.06	0.973
	50	1.722	8.32	1.42	0.647
	60	1.711	10.8	1.86	0.445

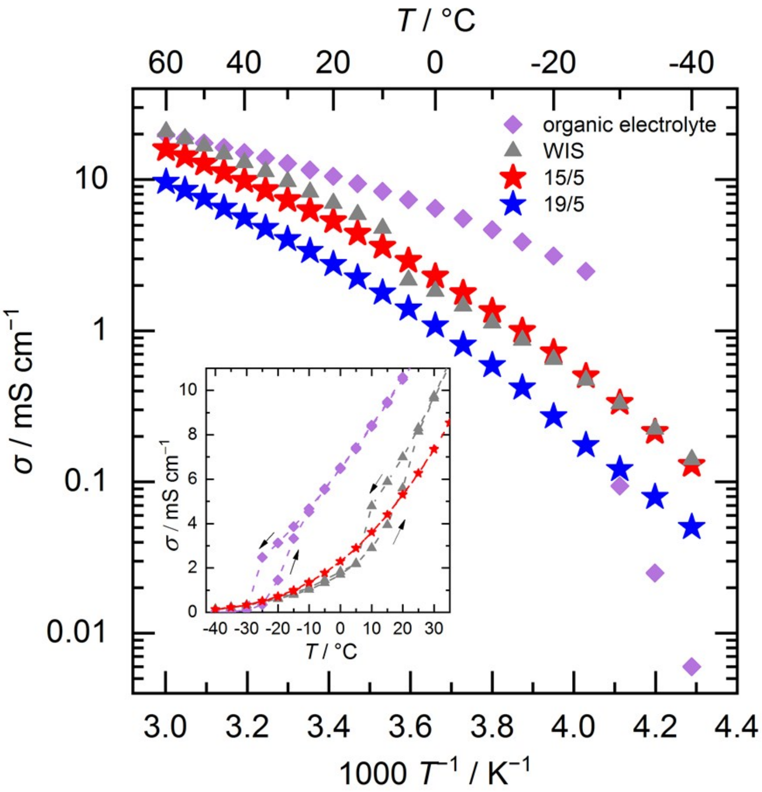

Figure S4: Temperature-dependent conductivity of selected water-in-salt electrolytes. The data was recorded during a cooling scan. For comparison, data for the organic electrolyte 1M $LiPF_6$ in EC:DMC 1:1 (v/v) is also shown. The inset additionally contains the heating scan data for selected electrolytes to illustrate the hysteresis found for the organic electrolyte and 21m LiTFSI (WIS).

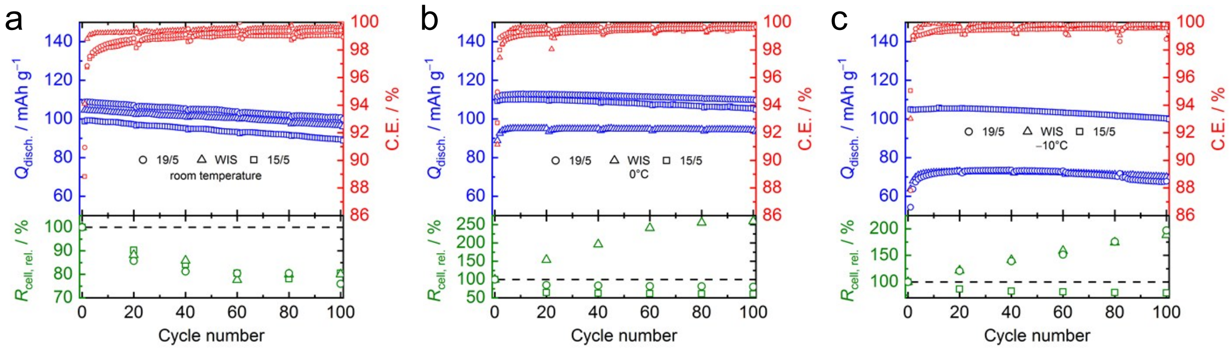

Figure S5: Galvanostatic cycling data for $LiMn_2O_4$ half cells recorded at 25 °C, 0 °C, and –10 °C. The cells were cycled at a rate of 1C. Activated carbon was used as counter electrode. The lower and upper cut-off potentials for the $LiMn_2O_4$ electrodes were set to 0.6 and 1.5 V vs. Ag/AgCl, respectively. Impedance spectra were recorded prior to cycling and after every 20 cycles, and the relative cell resistance ($R_{cell,\ rel.}$) was calculated as described above. The experiments were conducted for cells containing the LiPTFSI/LiOTf mixtures 19/5 and 15/5 as the electrolyte, respectively. For comparison, equivalent experiments were conducted using 21m LiTFSI (WIS) as the electrolyte.