Electronic Supplementary Material (ESI) for Energy & Environmental Science.
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Supporting information

Concentrated Mixed Cation Acetate "Water-in-Salt" Solutions as Green and Low Cost High Voltage Electrolytes for Aqueous Batteries

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1. Supplementary figures

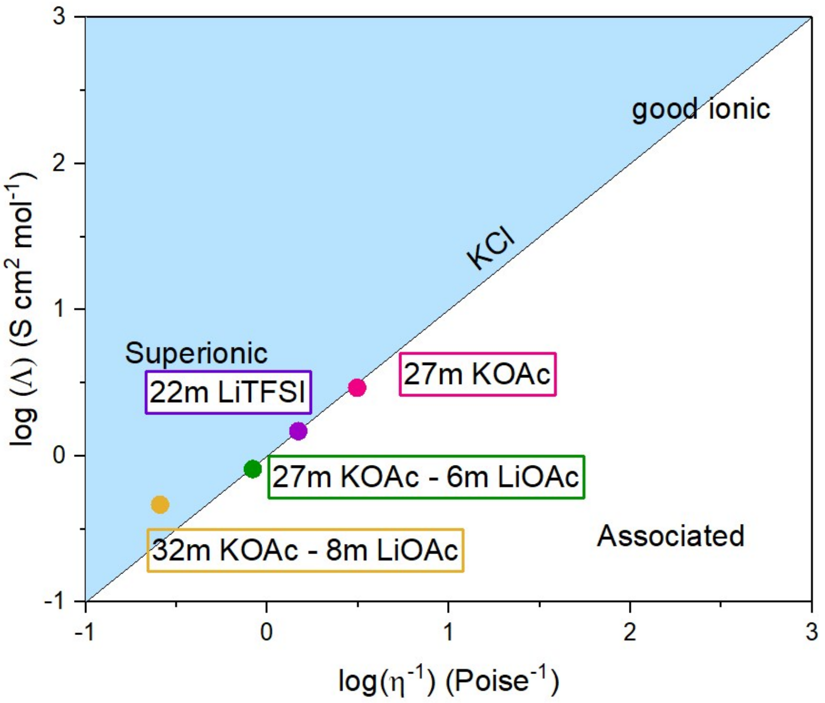

Figure S1. Walden plot for 27 m KOAc (pink closed circle), 27 m KOAc − 6 m LiOAc (green closed circles), 32 m KOAc − 8 m LiOAc (yellow closed circles) and 22 m LiTFSI (violet closed circle) at various concentrations at 25 °C. The Walden plot was generated from the molar conductivities (Λ) and viscosities (η) of the electrolyte solutions.

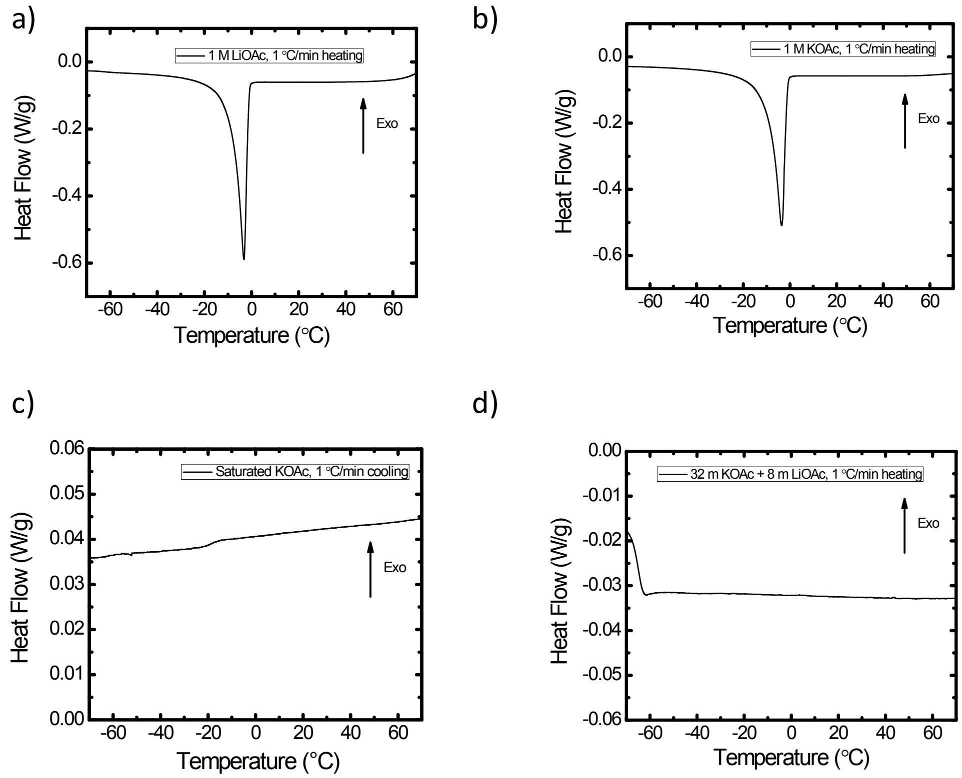

Figure S2. Differential scanning thermograms of a) 1 m LiOAc, b) 1 m KOAc, c) saturated aqueous KOAc, and d) the WIS solution of 32 m KOAc – 8 m LiOAc.

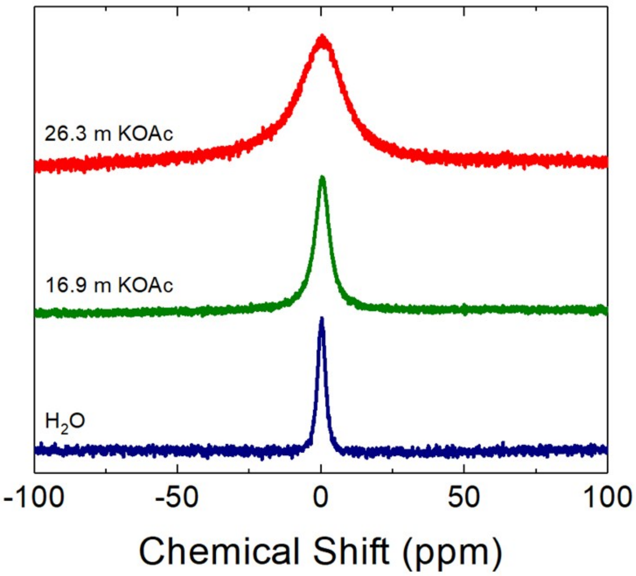

Figure S3. ^{17}O NMR spectra of KOAc solutions. Data are vertically offset and normalized to ease visualization.

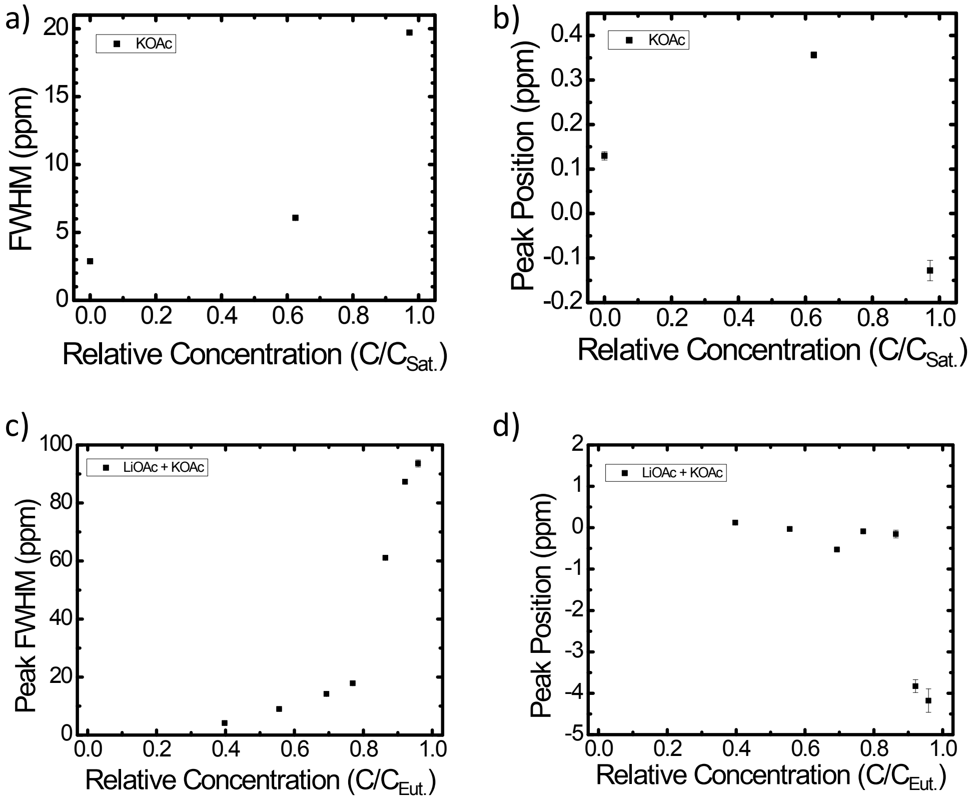

Figure S4. (a, b) Trends in ^{17}O NMR data of LiOAc solutions. Concentration is shown relative to saturation (27 m). (c, d) Trends in ^{17}O NMR data of LiOAc – KOAc solutions. Concentration is shown relative to the eutectic concentration, 32 m KOAc – 8 m LiOAc.

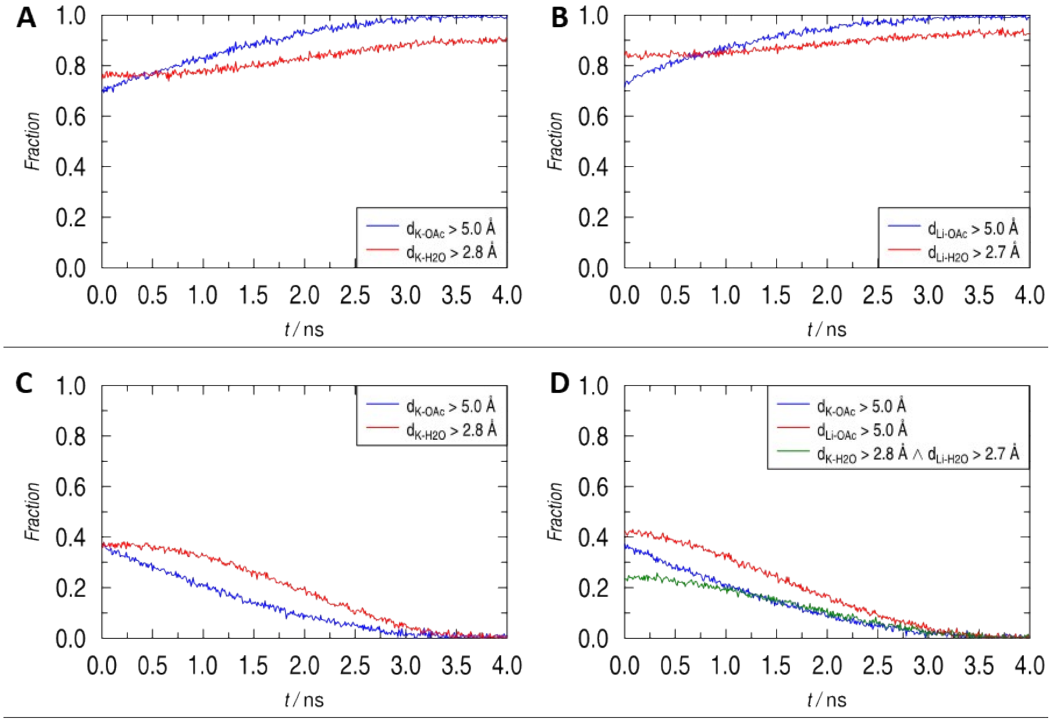

Figure S5: Illustration of the composition of the simulated electrolytes as a function of time. From top left to bottom right: (A) 1 m KOAc, (B) 1 m LiOAc, (C) 27 m KOAc, (D) 32 m KOAc−8 m LiOAc.

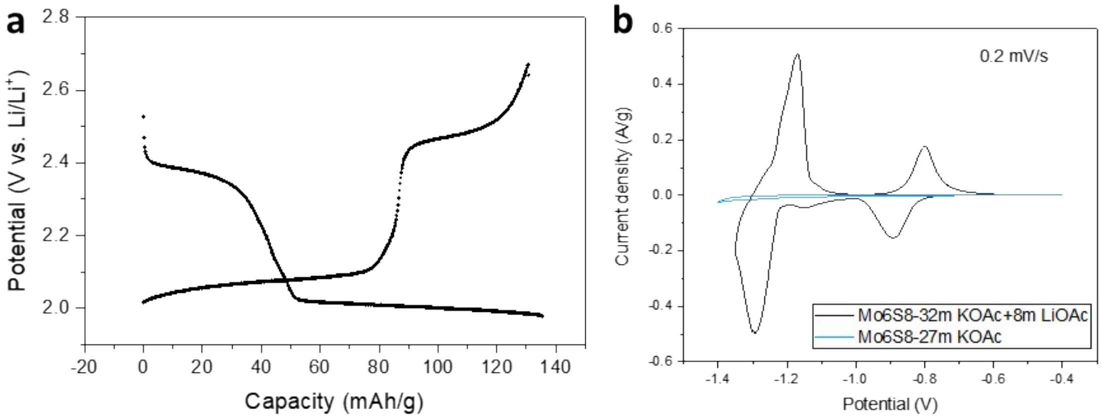

Figure S6. **a**, Galvanostatic charge/discharge profile collected at 0.2 A/g charging rate for Mo_6S_8 electrode in 32 m KOAc – 8 m LiOAc solution. **b**, Cyclic voltammetry profiles collected at scan rate of 0.2 mV/s for Mo_6S_8 electrodes in 27 m KOAc (blue line) and 32 m KOAc – 8 m LiOAc (black line) solutions.

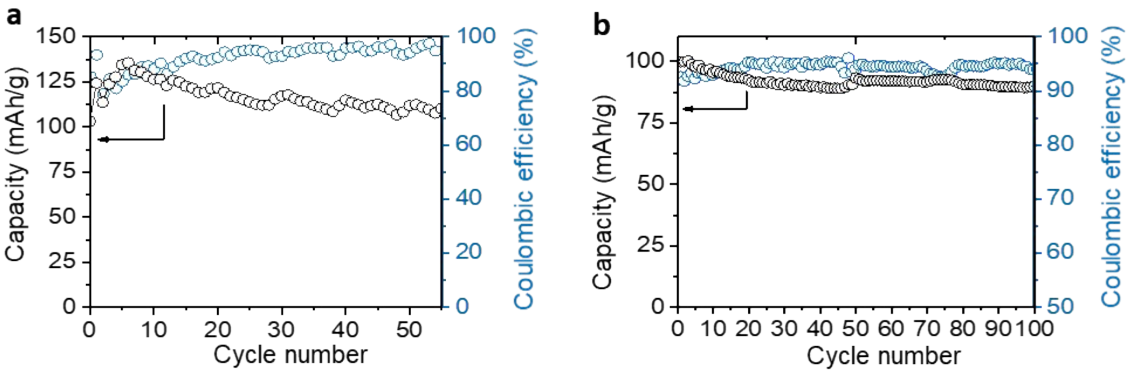

Figure S7. Capacity retention data and coulombic efficiency for a, c-TiO_2 and b, $LiMn_2O_4$ collected at 0.5 C charging rate.

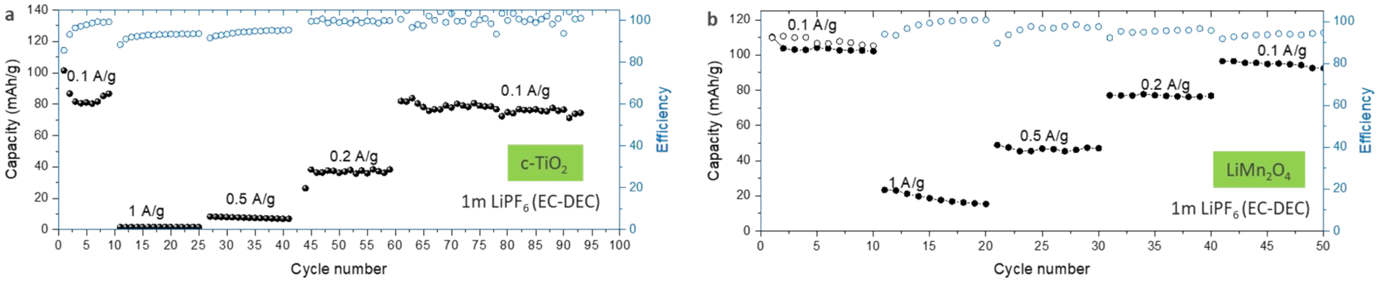

Figure S8. **Cycling stability and rate performance data** for **a**, c-TiO_2 anode and **b**, $LiMn_2O_4$ cathode in 1 m $LiPF_6$ (EC-DEC).

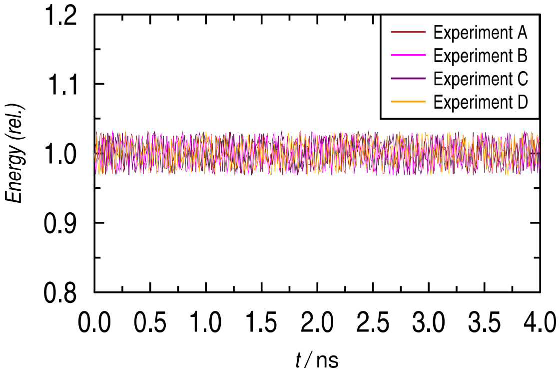

Figure S9: Illustration of the temporal evolution of the relative energy during the simulation for the systems (A)-(D).

Table S1. Composition of the electrolyte systems analyzed using MD.

System	**A**	**B**	**C**	**D**
Molarity	1 m KOAc	1 m LiOAc	27 KOAc	32 KOAc + 8 LiOAc
Ratio Water/KOAc Water/LiOAc	 55.5 -	 - 55.5	 2.1 -	 1.7 6.9
Number of Water molecules	333	333	231	187
Number of KOAc molecules	6	-	110	110
Number of LiOAc molecules	-	6	-	27

2. Supplementary text

MD simulation results of the acetate water-in-salt system

Experimental data as well as theoretical examinations consistently give the radius of the primary hydration shell of a K^+ ion in an aqueous 6-ligand environment as Hyd_K = 2.8 Å, and the hydration shell of Li^+ as Hyd_{Li} = 2.7 Å.[S1] It has to be noted that for Li^+ ion, the radius of the hydration shell is reported with more ambiguity, reflecting the transition from 4 to 6 coordinate Li^+ as well as the non-negligible impact of the second hydration shell on the solvation. Free water, defined as being outside of the hydration shells, can adsorb on the electrode surface. For mono-salt electrolytes, fractions of free water of 0.15 were reported,[S2] while for bi-salt systems mixing two lithium salts, fractions of free water as low as 0.11 were reached.[S3]

After the simulations of electrolytes A (1 m KOAc) and B (1 m LiOAc) reach a structurally stable state at 3 ns, the respective ions in the systems are fully separated by more than 5 Å (see **Figure S5 A and B**, blue), with no interpenetration of the hydration shells. As expected for the low salt concentrations, the bulk of the water molecules is present outside of the respective cationic hydration shells (Hyd_K = 2.8 Å and Hyd_{Li} = 2.7 Å), and the fraction of free water is around 0.9 for system A and 0.95 for system B. The difference reflects the higher average coordination number of the K^+ ion. The results of the simulations are in accordance with the expected behavior of the electrolytes A and B, which both represent classic salt-in-water systems.

In the simulation of system C, a potassium based electrolyte with a concentration of 27 m KOAc, the hydration shells show a high degree of interpenetration with all water molecules present in at least one hydration shell at any given time. The fraction free water ($d_{K\text{-}H2O} > 2.8$ Å) as well as the fraction of separated ion pairs ($d_{K\text{-}OAc} > 5$ Å) approaching 0 after 3 ns (see **Figure S5 C**), The fraction of free water is lower than the reported lithium based mono-salt electrolyte, which is consistent with the higher concentration (27 m KOAc as compared to 22 m LiTFSI) and the higher average coordination number of potassium.

For the highly concentrated mixed-cationic electrolyte D with 32 m KOAc − 8 m LiOAc, the fraction of free water, defined as being outside of a cationic hydration shell with radii $Hyd_K = 2.8$ Å and $Hyd_{Li} = 2.7$ Å is approaching 0 (see **Figure S5 D**, green) in the stable system reached after a simulation time of 3 ns. Also, the concentration yields a system with a markedly high degree of interpenetration of the hydration shells where the fraction of ions isolated by water is approximating 0 (see **Figure S5 D**, blue and red). Based on the MD simulations, the system can consequently be described as a near-ideal example of a water-in-salt electrolyte.

3. Supplementary references

S1. J. Mähler, I. Persson, *Inorganic Chemistry*, 2012, **51 (1)**, 425-438A

S2. L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang and K. Xu, *Science*, 2015, **350**, 938

S3. L. Suo, O. Borodin, W. Sun, X. Fan, C. Yang, F. Wang, T. Gao, Z. Ma, M. Schroeder, A. von Cresce, S. M. Russell, M. Armand, A. Angell, K. Xu and C. Wang, *Angewandte Chemie International Edition*, 2016, **55**, 7136-7141.