Hydrated Eutectic Electrolytes for High-performance Mg-ion Batteries

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1. Experimental Section

1.1 Synthesis of copper hexaferrocyanide (CuHCF).

Synthesis of CuHCF big nanoparticles. A typical co-precipitation method was used to fabricate the Cu-HCF big nanoparticles. 40 mM of Cu(NO₃)₂ aqueous solutions was mixed with 20 mM $K_3Fe(CN)_6$ in a dropwise manner. The mixture color was instantly changed to dark brown and CuHCF rapidly precipitated. The precipitates were collected by centrifugation, washed with distilled water, and then dried under vacuum at room temperature. The chemical composition of the CuHCF big nanoparticles, characterized by inductively coupled plasma mass spectrometry (ICP-MS), is determined to be Cu[Fe(CN)₆]_{0.73}.

Synthesis of CuHCF small nanoparticles. The key to control the particle size of CuHCF is to slow down the precipitation speed. To achieve so, we utilized the saturated aqueous solution of KCl (150 ml), which was further mixed with 3 mmol K₄Fe(CN)₆. The clear solution with then mixed with 6 mmol Cu(NO₃)₂ (150 ml) under vigorous stirring. The mixture was aged at room temperature for 6 h to have the precipitates. The precipitates were collected, washed, and dried under vacuum at room temperature. The chemical composition of the CuHCF small nanoparticles, analyzed by ICP-MS, is determined to be Cu[Fe(CN)₆]_{0.71}.

In-situ Synthesis of Single Crystals from the Electrolytes. The single crystals discussed in the manuscript were in-situ generated from the electrolytes. Typically, the electrolytes were kept in vacuum for 1 day and the slightly wet crystals were instantly transferred to the cold nitrogen stream on the single-crystal XRD instrument.

1.2. Materials Characterizations.

Transmission electron microscopy (TEM) images were recorded on an FEI Titan CT electron microscope operated at 300 kV, respectively. To prepare the samples for TEM imaging, 1 mg of electrode materials was dispersed into 2 ml ethanol under sonication. Then 2 μ l of the homogeneous suspension was dropcast

onto a copper grid covered with a carbon film and dried overnight under vacuum. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance powder diffractometer at 40 kV and 40 mA using Co-Kα radiation. Attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer (32 scans, resolution: 4 cm⁻¹). All liquid-state NMR spectra were recorded using a Bruker 600 MHz AVANACIII NMR spectrometer equipped with BBO probe (BrukerBioSpin, Rheinstetten, Germany). Raman spectra were recorded on a micro-Raman spectrometer (LabRAM ARAMIS, Horiba-Jobin Yvon) with notch filters cutting at 100 cm⁻¹ with the use of a laser wavelength of 532 nm. The liquid electrolytes and water were tightly sealed in qaurtz cuvettes during Raman measurements. Ionic conductivity was performed on an Oaktont CON 6⁺ conductivity meter at room temperature. Prior to each measurement, the calibration was conducted in 20 and 50 mS cm⁻¹ calibration solution (HI7030L by Hanna Instruments). Viscosity measurements were recorded on an oscillatory rheometer (ARES-G2, TA Instruments) at room temperature. 1 mL of the solution was added to a sample cup, and the sample was analyzed in a cone and cup geometry. Singlecrystal structure data acquisition was performed on Bruker D8 Venture single-crystal X-ray diffractometer at 120 K with Mo-Ka radiation ($\lambda = 0.71073$ Å). The crystalline structures were determined by SHELXT using the Olex2 software package. The non-hydrogen atoms can be determined from difference Fourier maps and refined by full-matrix least-squares methods. Hydrogen atoms are added using HFIX command.

1.3. Electrochemical Measurements.

A slurry was first made using 70% active materials, 20% conductive carbon black, and 10% polyvinylidene difluoride (PVDF) binder in *N*-methyl-2-pyrrolidone (NMP). The homogeneous slurry was then cast onto a Ti foil using a doctor blading method, followed by drying in a vacuum oven at 60 °C. The mass loading of active materials was ~4 mg cm⁻². Noticeably, PTCDA was purchased and used as-received from Sigma-Aldrich. A conventional three-electrode setup was used to evaluate the electrochemical performance of the PTCDA anode or the CuHCF cathode using an Ag/AgCl reference

electrode and a counter electrode of activated carbon. For the full battery, CR2032 coin cells were assembled by stacking the cathode and anode separated by glass fiber. All electrochemical (e.g., galvanostatic charge-discharge testing) tests were performed on a VMP3 Biologic potentiostat (Biologic, France). We further conducted *ex-situ* characterization techniques to analyze the changes of structures or physicochemical states of the electrode materials. Galvanostatic charge-discharge tests at a current density of 1 C were performed. Upon approaching the pre-set potential, the three-electrode cell was then disassembled in a glovebox. The electrode was washed with 1,2-dimethoxyethane (DME) multiple times and then dried in the glovebox. To avoid sample oxidation during *ex-situ* experiments, the electrode was sealed with calcium fluoride window and very thin Parafilm for FT-IR and XRD, respectively.

1.4. Molecular Dynamics (MD) Simulations of the Bulk Electrolytes.

MD simulations were conducted for the mixtures with $n_{Mg2+}:n_{acetamide} = 1:2, 1:8, and 1;12$. The simulation cells contain 100 Mg(NO₃)₂, 600 H2O, and 200 acetamide for $n_{Mg2+}:n_{acetamide} = 1:2, 100 Mg(NO_3)_2, 600$ H₂O, and 800 acetamide for n_{Mg2+} : $n_{acetamide} = 1:8$, and 100 Mg(NO₃)₂, 600 H₂O, and 1200 acetamide for n_{Mg2+} : $n_{acetamide} = 1:12$. All of the 0.8 scale OPLS-AA force field parameters of ions were obtained from the previous report.^[S1] Others molecules were optimized using Gaussian 16 software with a level of B3LYP/def2tzvp. The OPLS-AA force field parameters were obtained from Ligpargen web server.^{[S2-} ^{S4]}. Additionally, the RESP2 charge was used to make the simulations more accurate.^[S5] The initial structures were modelled via Packing Optimization for MD simulations (Packmol) program.^[S6] The simulation boxes were set to $5 \times 5 \times 5$ nm³. All molecular dynamic simulations were performed via Gromacs software version 2019.5, and the simulation processes are:^[S7,S8]: The simulation process was detailed as following: the 5000-step steepest descent method and 5000-step conjugate gradient method were used to avoid unreasonable contact of system. NPT ensemble was used to pre-equilibrate the system, and V-rescale temperature coupling and parrinello-rahman pressure coupling were used to set the temperature at 298 K, the pressure was maintained at 1 atm, the non-bonding cutoff radius was 1.2 nm, and the integration step was 1 fs. The systems were then heated from 298 to 500 K for 1 ns, and

maintained at 500 K for 1 ns, and subsequently annealed from 500 to 298 K in 1 ns. After that, the simulation boxes were equilibrated at 298 K in an NPT ensemble for another 1 ns. A 15-ns production run in an NVT ensemble under Nose-Hoover thermostat with a time constant of 1 ps at 298 K was finally conducted. Only the final 5 ns was sampled for radial distribution function (RDF) and coordination structure counting analyses. A time step of 1 fs was used for all simulations.

2. Supplementary Fig.s.



Fig. S1 Cycling stability test (a) of the PTCDA electrode and the corresponding galvanostatic chargedischarge curves (b) in saturated $Mg(NO_3)_2$ aqueous electrolytes (current rate: 10 C). The fast capacity degradation is related to the dissolution of the organic-molecule PTCDA electrode during cycling in aqueous electrolytes.^[S9,S10]



Fig. S2 Optical photos of the transparent eutectic electrolyte with $n_{Mg2+}:n_{acetamide} = 1:8$ before and after 10-month storage.



Fig. S3 Physical property summary of the mixture of Mg(NO₃)₂·6H₂O and acetamide at different molar ratios. At $n_{Mg2+}:n_{Acetamide} = 1:2$, the mixture of Mg(NO₃)₂·6H₂O and acetamide shows a high ionic conductivity of 8.85 mS cm⁻¹ and a viscosity of 78.1 mPa s. Both viscosity and ionic conductivity decrease upon decreasing $n_{Mg2+}:n_{Acetamide}$. The mixture of Mg(NO₃)₂·6H₂O and acetamide with $n_{Mg2+}:n_{Acetamide} = 1:12$ shows the lowest ionic conductivity of 4.53 mS cm⁻¹ and the lowest viscosity of 54.6 mPa s.



Fig. S4 Electrochemical stability windows of two representative electrolytes (scan rate: 1 mV s⁻¹).



Fig. S5 Structural analysis of the PTCDA anode. (a,b) Crystalline structure, and (c-e) TEM images. The sufficient space within the PTCDA anode is beneficial for reversible Mg²⁺ intercalation.^[S10]



Fig. S6 *Ex-situ* FT-IR spectra of the PTCDA anode using the eutectic electrolyte with $n_{Mg2+}:n_{acetamide} =$ 1:8. During charge and discharge, the reversible changes of stretching vibrations of C=O and -COOOC- and deformation vibration of C=O indicate the redox-active nature of C=O upon Mg²⁺ (de)insertion.^[S10,S11] The other typical features of PTCDA remain to be stable during charge and discharge, revealing its flexible and stable framework in this hydrated eutectic formulation.



Fig. S7 Cycling stability tests of the PTCDA anode in the hydrated eutectic electrolytes with $n_{Mg2+}:n_{acetamide} = 1:4$ and 1:6, showing faster capacity degradation compared to that of $n_{Mg2+}:n_{acetamide} = 1:8$. This should be related to the much decreased amount of water molecules to suppress electrode dissolution.



Fig. S8 Galvanostatic charge-discharge curves of the PTCDA electrode using the hydrated eutectic electrolytes ($n_{Mg2+}:n_{acetamide} = 1:8$): pristine (pH =7) and mildly acidic (adding dilute HNO₃ to adjust pH to 5). The redox potential of the PTCDA electrode does not depend on the pH and the voltage profiles overlap, indicating that Mg²⁺ instead of H⁺ is the cation being (de)intercalated.^[S11,S12] This is reasonable because of the significantly suppressed water activity, as already confirmed by different techniques.



Fig. S9 Raman spectra of the electrolytes. Compared to pure water and 1 M Mg(NO₃)₂ aqueous solution, ee notice that for the hydrated eutectic electrolytes, there are significant changes for the O–H stretching modes of water clusters in the range of 3000–3800 cm⁻¹. Acetamide shows typical vibrations in nearly the same range, which may complicate the detailed analysis. However, it is noteworthy that upon decreasing n_{Mg2+} : $n_{acetamide}$, the Raman signal at ~1060 cm⁻¹ decreases with the intensity increase of the peak at ~1124 cm⁻¹. This is a typical feature of nondegenerate modes of vibrations that are assigned to the three different hydrates (*i.e.*, Mg²⁺–H₂O),^[S13,S14] whereas the hydration number is decreasing. This indicates that acetamide start replacing water molecules in the solvation sheath of Mg²⁺ upon increasing the content of acetamide.



Fig. S10 ¹H PFG-NMR spectrum of the mixture with $n_{Mg2+}:n_{acetamide} = 1:12$.



Fig. S11 Liquid-state ¹H NMR spectra of the mixtures with different molar ratios and the standard sample of 1M Mg(NO₃)₂. Upon increasing the content of acetamide, ¹H resonance signals of acetamide shows more pronounced shift compared to that of H₂O. This is a strong indication of the domination of acetamide molecules in the solvation sheath of Mg²⁺.



Fig. S12 (a) Snapshot of the MD simulation cell for the mixture of $n_{Mg2^+}:n_{acetamide} = 1:2$ (right: representative Mg²⁺-solvation structure). (b) RDF plots of Mg²⁺-H₂O, Mg²⁺-acetamide, and Mg²⁺-NO₃⁻ (i.e., RDFs plots of Mg²⁺ to the centroids of different species). The simulation results of the solvation structure of Mg²⁺ show that the primary solvation sheath is still dominated by water, as further confirmed by the RDF analysis. (c) More representative Zn²⁺ solvation structures.



Fig. S13 (a) Snapshot of the MD simulation cell for the mixture of $n_{Mg2^+}:n_{acctamide} = 1:8$ (right: representative Mg²⁺-solvation structure). (b) RDF plots of Mg²⁺-H₂O, Mg²⁺-acctamide, and Mg²⁺-NO₃⁻. Many water clusters can be observed in the MD simulation cell. The simulation results of the solvation structure of Mg²⁺ show that the first solvation sheath is gradually substituted by acctamide molecules upon decreasing $n_{Mg2^+}:n_{acctamide}$, as further confirmed by the RDF analysis. (c) More representative Zn²⁺ solvation structures.



Fig. S14 (a) Snapshot of the MD simulation cell for the mixture of $n_{Mg2+}:n_{acetamide} = 1:12$ (right: representative Mg²⁺-solvation structure). (b) RDF plots of Mg²⁺-H₂O, Mg²⁺-acetamide, and Mg²⁺-NO₃⁻. A lot of acetamide clusters can be seen in the MD simulation cell. The simulation results of the solvation structure of Mg²⁺ show that the first solvation sheath is still dominated by acetamide molecules, as further confirmed by the RDF analysis. (c) More representative Zn²⁺ solvation structures.



Fig. S15 MD simulation results for the electrolyte with $n_{Mg2+}:n_{acetamide} = 1:2$. (a) Hydrogen bond networks of H₂O-NO₃⁻. (b) Hydrogen bond networks of H₂O-Acetamide. (c) RDFs plots of H2O-O and the corresponding coordination environments of O (H₂O). (d) Representative composition evolutions of the first solvation sheath of Mg²⁺ during MD simulations. Combining with Fig. S16 and S17, we find that more percolating hydrogen bond networks of H₂O-acetamide start to form upon increasing the molar ratio of acetamide in the electrolytes, while the hydrogen bond networks of H₂O-NO₃⁻ gradually break up. Importantly, RDFs plots reveal that the coordination sheath of H₂O is gradually dominated by acetamide molecules without breaking the hydrogen bond networks of H₂O-H₂O. There are critical features of suppressing water activity and ensuring decent ionic conductivity.



Fig. S16 MD simulation results for the electrolyte with $n_{Mg2+}:n_{acetamide} = 1:8$. (a) Hydrogen bond networks of H₂O-NO₃⁻. (b) Hydrogen bond networks of H₂O-Acetamide. (c) RDFs plots of H2O-O and the corresponding coordination environments of O (H₂O). (d) Representative composition evolutions of the first solvation sheath of Mg²⁺ during MD simulations.



Fig. S17 MD simulation results for the electrolyte with $n_{Mg2+}:n_{acetamide} = 1:12$. (a) Hydrogen bond networks of H₂O-NO₃⁻. (b) Hydrogen bond networks of H₂O-Acetamide. (c) RDFs plots of H2O-O and the corresponding coordination environments of O (H₂O). (d) Representative composition evolutions of the first solvation sheath of Mg²⁺ during MD simulations.



Fig. S18 Single-crystal XRD analysis the mixture with $n_{Mg2+}:n_{acetamide} = 1:2$. (a) The structure obtained from single-crystal XRD and (b) the corresponding transparent crystal. Single-crystal result shows that Mg^{2+} is coordinated by six water molecules, which are surrounded by acetamide and nitrate. This indicates that the first solvation sheath is dominated by water molecules, which is consistent with the MD simulations and spectroscopy characterizations.



Fig. S19 Single-crystal XRD analysis the mixture with $n_{Mg2+}:n_{acctamide} = 1:8$. (a) The structure obtained from single-crystal XRD and (b) the corresponding transparent crystal. The crystalline structure reveals that Mg^{2+} is coordinated by two water molecules and four acetamide molecules, while two nitrate anions exist to ensure the charge balance. This signifies that the first solvation shell of this hydrated eutectic formuation is dominated by acetamide molecules, which is in good agreement with the MD simulations and spectroscopy results.



Fig. S20 Single-crystal XRD analysis the mixture with $n_{Mg2+}:n_{acetamide} = 1:12$. (a) The structure obtained from single-crystal XRD and (b) the corresponding transparent crystal. This composition show nearly the same crystal structure to that of $n_{Mg2+}:n_{acetamide} = 1:12$. This is a strong indication of that the excess amount of acetamide molecules exist in the form of clusers without strong interaction with Mg^{2+} ions, as confirmed by MD simulations and spectroscopy analysis.



Fig. S21 Structure analysis of the Cu-HCF cathode. (a) Crystal structure and (b) power XRD patterns. The A sites of the Cu-HCF cathode can accommodate Mg²⁺ efficiently and reversibly. The XRD patterns confirms the efficiency of our strategies in decreasing the size of Cu-HCF without changing the crystallize structure.



Fig. S22 TEM images and the corresponding selected-area electron diffraction (SAED) patterns of Cu-HCF. (a-c) Big nanoparticles and (d-f) small nanoparticles. The particle size can be efficiently reduced from 100-200 nm to 20-40 nm using our chemical strategies (see Experimental details) without changing the crystalline structure, as confirmed by SEAD patterns (Fig. S17c,f).



Fig. S23 Rate performance comparison of the two Cu-HCF cathodes. This indicates that decreasing the particle size can efficiently improve the diffusion, thus leading to an improved rate capability.^[S14]



Fig. S24 *Ex-situ* XRD analysis of the Cu-HCF cathode (small nanoparticles) during charge and the magnified region of the XRD patterns shows the reversible changes of the 020 diffraction during charge and discharge. The Cu-HCF electrode maintains its face-centered cubic structure over the whole process of charge and discharge. However, the diffractions shift to higher degrees upon Mg²⁺ intercalation and a reversible lattice recovery after full removal upon recharge. This reversible structural change is related to the combined effect of shortened Fe–N distance on potassiation and smaller ionic diameter of $[Fe(CN)_6]^{4-}$ compared to $[Fe(CN)_6]^{3-}.[S16-S18]$



Fig. S25 Ragone plots of energy density *vs.* power density (calculated based on the mass of active cathode and anode), showing the comparison of our aqueous MIB chemistry with the state-of-the-art aqueous Mg-ion batteries.



Fig. S26 The cycling performance test of the full MIB at 8 C using the PTCDA anode, CuHCF cathode, and the hydrated eutectic electrolyte with the formulation of $n_{Mg2+}:n_{acetamide} = 1:8$.



Fig. S27 FT-IR spectra of the hydrated eutectic electrolyte ($n_{Mg2+}:n_{acetamide} = 1:8$) after 50 cycles of the full battery (current rate: 5C), showing the stability of our hydrated eutectic electrolyte to withstand multiple charge-discharge tests.

3. Supplementary Tables.

Lattice type					Р	P					
Space group name					P -1	P -1					
Space group number					2	2					
Setting number					1	1					
Temperature					120 K						
Unit-cell volume					419.199	720 Å ³					
Lattice parameters											
<i>a</i> (Å)		<i>b</i> (Å)	<i>c</i> (Å)		alpha (°)		beta (°)	gam	ma (°)		
6.40950		6.49770	10.94140		84.9520		79.7060	69.2830			
			x	у	Ζ	Occ.	U	Site	Sym.		
1	Mg	Mg01	0	0.5	0.5	1	0.016	1g	-1		
2	0	O002	0.32805	0.35572	0.52442	1	0.022	2i	1		
3	Н	H00A	0.37835	0.33343	0.59306	1	0.033	2i	1		
4	Н	H00B	0.44317	0.29532	0.47093	1	0.033	2i	1		
5	0	O003	0.07641	0.34476	0.33089	1	0.023	2i	1		
6	Н	H00C	0.21157	0.29347	0.29353	1	0.035	2i	1		
7	Н	H00D	0.01859	0.24925	0.32118	1	0.035	2i	1		
8	0	O004	0.51133	0.22867	0.19311	1	0.024	2i	1		
9	0	O005	0.06633	0.76889	0.41245	1	0.024	2i	1		
10	Н	H00E	0.18447	0.77191	0.3638	1	0.036	2i	1		
11	Н	H00F	-0.03776	0.88443	0.39293	1	0.036	2i	1		
12	0	O006	0.4649	0.74371	0.27156	1	0.026	2i	1		
13	0	O007	0.87565	0.09668	0.15596	1	0.031	2i	1		
14	0	O008	0.70625	0.15602	0.3454	1	0.029	2i	1		
15	Ν	N009	0.69677	0.15934	0.23177	1	0.018	2i	1		
16	Ν	N00A	0.34905	0.80287	0.08538	1	0.024	2i	1		
17	Н	H00G	0.20945	0.8539	0.11895	1	0.029	2i	1		
18	Н	H00H	0.38448	0.79549	0.00587	1	0.029	2i	1		
19	С	C00B	0.50974	0.73553	0.15622	1	0.018	2i	1		
20	С	COOC	0.74883	0.65066	0.09056	1	0.025	2i	1		
21	Н	H00I	0.78212	0.7664	0.03936	1	0.038	2i	1		
22	Н	H00J	0.7679	0.53042	0.03955	1	0.038	2i	1		
23	Н	H00K	0.84959	0.60081	0.15071	1	0.038	2i	1		

Table S1. Crystal data for the single crystal obtained from the mixture with $n_{Mg2+}:n_{acetamide} = 1:2$.

Lattice type P											
Space group name					P -1	P-1					
Space group number					2	2					
Setting number					1	1					
Temperature					120 K	120 K					
Unit-cell volume					653.231	653 231547 Å ³					
Lattice parameters											
a (Å)	b (Å)	c ()	<u>Å)</u>	alpha (°) beta (°)			gamma (°)			
7.28170		9.21760	10.69880		81.0560		73.7150	71.8	690		
<u></u>											
			x	у	Z	Occ.	U	Site	Sym.		
1	Mg	Mg1	0.5	0.5	0.5	1	0.025	1h	-1		
2	0	O1	0.65688	0.64028	0.53237	1	0.03	2i	1		
3	0	O2	0.61333	0.32999	0.63755	1	0.03	2i	1		
4	0	O3	0.25764	0.59879	0.64356	1	0.031	2i	1		
5	Н	H3A	0.23889	0.53137	0.70903	1	0.046	2i	1		
6	Н	H3B	0.28382	0.66906	0.67591	1	0.046	2i	1		
7	0	O4	0.1056	0.4146	0.84392	1	0.035	2i	1		
8	0	05	0.4573	0.91661	0.83676	1	0.052	2i	1		
9	0	O6	0.2756	0.86614	0.72953	1	0.037	2i	1		
10	0	07	0.4032	0.69624	0.86774	1	0.056	2i	1		
11	Ν	N1	0.63502	0.84391	0.38597	1	0.035	2i	1		
12	Н	H1A	0.56166	0.81238	0.34922	1	0.041	2i	1		
13	Η	H1B	0.6664	0.92974	0.35568	1	0.041	2i	1		
14	Ν	N2	0.37928	0.82688	0.81178	1	0.03	2i	1		
15	С	C1	0.8221	0.82157	0.5452	1	0.035	2i	1		
16	Н	H1C	0.7552	0.83856	0.6371	1	0.053	2i	1		
17	Н	H1D	0.83966	0.91824	0.49797	1	0.053	2i	1		
18	Н	H1E	0.9528	0.74622	0.53923	1	0.053	2i	1		
19	С	C2	0.69766	0.76292	0.48596	1	0.026	2i	1		
20	С	C3	0.72999	0.30807	0.70912	1	0.027	2i	1		
21	С	C4	0.7831	0.15743	0.78677	1	0.037	2i	1		
22	Н	H4A	0.66149	0.13781	0.84501	1	0.055	2i	1		
23	Н	H4B	0.87299	0.16073	0.83876	1	0.055	2i	1		
24	Н	H4C	0.84951	0.07545	0.72721	1	0.055	2i	1		
25	Ν	N5	0.81034	0.41368	0.71951	1	0.036	2i	1		
26	Н	H5A	0.7824	0.50316	0.67521	1	0.044	2i	1		
27	Н	H5B	0.89209	0.39492	0.77075	1	0.044	2i	1		
28	С	C6	0.1364	0.21614	1.01554	1	0.045	2i	1		
29	Н	H6A	-0.00718	0.24488	1.05603	1	0.068	2i	1		
30	Н	H6B	0.20992	0.18616	1.08379	1	0.068	2i	1		
31	Н	H6C	0.17078	0.12999	0.96187	1	0.068	2i	1		
32	С	C7	0.191	0.34961	0.93142	1	0.029	2i	1		
33	Ν	N8	0.3331	0.39493	0.95417	1	0.036	2i	1		
34	Н	H8A	0.36937	0.47299	0.90675	1	0.044	2i	1		
35	Н	H8B	0.39146	0.34706	1.01674	1	0.044	2i	1		

Table S2. Crystal data for the single crystal obtained from the eutectics with $n_{Mg2+}:n_{acetamide} = 1:8$.

Lattice type P											
Space group name					P -1	<u> </u>					
Space group number					2	2					
Setting number					1						
Tem	perature	;			120 K	120 K					
Unit	cell vol	ume			655.202	2826 Å ³					
				Lattice	parameters	3					
a (Å	.)	<i>b</i> (Å)	<i>c</i> (Å)		alpha (°)		beta (°)	gam	ma (°)		
7.29020		9.22420	10.71000		81.0550		73.7310	71.8	710		
			x	у	Ζ	Occ.	U	Site	Sym.		
1	Mg	Mg01	0.5	0.5	0.5	1	0.023	1h	-1		
2	0	O002	0.6568	0.64	0.53245	1	0.028	2i	1		
3	0	O003	0.61328	0.32993	0.63749	1	0.028	2i	1		
4	0	O004	0.25719	0.59865	0.64352	1	0.028	2i	1		
5	Н	H00A	0.23882	0.53301	0.70792	1	0.043	2i	1		
6	Н	H00B	0.28212	0.6679	0.67511	1	0.043	2i	1		
7	0	O005	0.10571	0.41464	0.84383	1	0.032	2i	1		
8	0	O006	0.2757	0.86622	0.72939	1	0.035	2i	1		
9	0	O007	0.457	0.91638	0.83706	1	0.049	2i	1		
10	Ν	N008	0.37906	0.82679	0.81196	1	0.028	2i	1		
11	0	O009	0.4035	0.6962	0.86765	1	0.054	2i	1		
12	Ν	N00A	0.33328	0.39497	0.95418	1	0.033	2i	1		
13	Н	H00M	0.34551	0.4721	0.90693	1	0.05	2i	1		
14	Ν	N00B	0.63502	0.84389	0.38621	1	0.032	2i	1		
15	Ν	N00C	0.81022	0.41369	0.71926	1	0.034	2i	1		
16	Н	H00E	0.88408	0.38038	0.7688	1	0.051	2i	1		
17	С	C00D	0.69764	0.76313	0.48582	1	0.023	2i	1		
18	С	C00E	0.73008	0.30808	0.70906	1	0.024	2i	1		
19	С	C00F	0.1911	0.34941	0.93141	1	0.026	2i	1		
20	С	C00G	0.8219	0.82179	0.54531	1	0.032	2i	1		
21	Н	H00G	0.755	0.84024	0.63476	1	0.048	2i	1		
22	Н	H00H	0.84121	0.91543	0.49813	1	0.048	2i	1		
23	Н	H00I	0.94877	0.7472	0.54109	1	0.048	2i	1		
24	С	C00H	0.7832	0.15757	0.78679	1	0.034	2i	1		
25	Н	H00J	0.66403	0.12896	0.83105	1	0.052	2i	1		
26	Н	H00K	0.84943	0.16697	0.8497	1	0.052	2i	1		
27	Н	H00L	0.86991	0.08061	0.72928	1	0.052	2i	1		
28	С	C00I	0.1368	0.21629	1.0152	1	0.043	2i	1		
29	Н	H00O	-0.00374	0.24436	1.05472	1	0.065	2i	1		
30	Н	H00P	0.20858	0.18699	1.08205	1	0.065	2i	1		
31	Н	H00Q	0.17054	0.13195	0.96267	1	0.065	2i	1		
32	Н	H00N	0.388	0.341	1.014	1	0.05	2i	1		
33	Н	H00C	0.659	0.94	0.356	1	0.049	2i	1		
34	Н	H00D	0.556	0.815	0.355	1	0.05	2i	1		
35	Н	H00F	0.775	0.505	0.668	1	0.058	2i	1		

Table S3. Crystal data for the single crystal obtained from the mixture with $n_{Mg2+}:n_{acetamide} = 1:12$.

 Table S4. Price comparison of different electrolytes.^a

Electrolyte	Price (USD g ⁻¹)
1.0 M LiPF ₆ in EC/DMC (50/50)	1.03
21m LiTFSI ("Water-in-salts") ^[S19]	5.85
Li(TFSI) _{0.7} (BETI) _{0.3} ·2H ₂ O (Hydrate melt) ^[S20]	11.7
Li-PAA-H ₂ O ("Water-in-ionomer") ^[S21]	0.26
LiTFSI-PEG-H ₂ O (Molecular crowding) ^[S22]	2.51
This work (Hydrated eutectic electrolyte)	0.18

^a Price of all the electrolytes was calculated based on the largest package size by Sigma-

Aldrich except the chemical of LiBETI (TCI).

4. Supplementary References

- S1. S. V. Sambasivarao, O. Acevedo, J. Chem. Theory Comput. 2009, 5, 4, 1038–1050.
- S2. W. L. Jorgensen, J. Tirado-Rives, Proc. Nat. Acad. Sci. U.S.A. 2005, 102, 6665–6670.
- S. Dodda, J. Z. Vilseck, J. Tirado-Rives, W. L. Jorgensen, J. Phys. Chem. B 2017, 121, 3864– 3870.
- S4. L. S. Dodda, I. Cabeza de Vaca, J. Tirado-Rives, W. L. Jorgensen, *Nucleic Acids Res.* 2017, 45, W331–W336.
- S5. M. Schauperl, P. S. Nerenberg, H. Jang, L.-P. Wang, C. I. Bayly, D. L. Mobley, M. K. Gilson, *Commun. Chem.* 2020, *3*, 44.
- S6. L. Martínez, R. Andrade, E. G. Birgin, J. M. Martínez, J. Comput. Chem. 2009, 30, 2157–2164.
- S7. H. Yang, X. Chen, N. Yao, N. Piao, Z. Wang, K. He, H.-M. Cheng, F. Li, ACS Energy Lett. 2021, 6, 1413–1421.
- S8. J. Fu, X. Ji, J. Chen, L. Chen, X. Fan, D. Mu, C. Wang, Angew. Chem. Int. Ed. 2020, 59, 22194– 22201.
- S9. L. Jiang, Y. Lu, C. Zhao, L. Liu, J. Zhang, Q. Zhang, X. Shen, J. Zhao, X. Yu, H. Li, X. Huang, L.
 Chen, Y.-S. Hu, *Nat. Energy* 2019, *4*, 495–503.
- S10. I. A. Rodríguez-Pérez, Y. Yuan, C. Bommier, X. Wang, L. Ma, D. P. Leonard, M. M. Lerner, R.
 G. Carter, T. Wu, P. A. Greaney, J. Lu, X. Ji, J. Am. Chem. Soc. 2017, 139, 13031–13037.
- S11. S. Gheytani, Y. Liang, F. Wu, Y. Jing, H. Dong, K. K. Rao, X. Chi, F. Fang, Y. Yao, *Adv. Sci.* 2017, *4*, 1700465.
- S12. Y. Liang, Y. Jing, S. Gheytani, K.-Y. Lee, P. Liu, A. Facchetti, Y. Yao, *Nat. Mater.*, 2017, 16, 841.
- S13. F. D'Amico, B. Rossi, G. Camisasca, F. Bencivenga, A. Gessini, E. Principi, R. Cucini, C. Masciovecchio, *Phys. Chem. Chem. Phys.* 2015, 17, 10987–10992.

- S14. T. G. Chang, D. E. Irish, J. Phys. Chem. 1973, 77, 52–57.
- S15. C. Choi, D. S Ashby, D. M Butts, R. H. DeBlock, Q. Wei, J. Lau, B. Dunn, *Nat. Rev. Mater.* 2020, 5, 5–19.
- S16. C. D. Wessells, S. V. Peddada, R. A. Huggins, Y. Cui, Nano Lett. 2011, 11, 5421–5425.
- S17. D. Su, A. McDonagh, S.-Z. Qiao, G. Wang, Adv. Mater. 2017, 4, 1604007.
- S18. X. Wu, J. J. Hong, W. Shin, L. Ma, T. Liu, X. Bi, Y. Yuan, Y. Qi, T. W. Surta, W. Huang, J. Neuefeind, T. Wu, P. A. Greaney, J. Lu, X. Ji, *Nat. Energy* 2019, *4*, 123–130.
- S19. L. Suo, O. Borodin, T. Gao, M. Olguin, J. Ho, X. Fan, C. Luo, C. Wang, K. Xu, Science 2015, 350, 938–943.
- S20. Y. Yamada, K. Usui, K. Sodeyama, S. Ko, Y. Tateyama, A. Yamada, Nat. Energy 2016, 1, 16129.
- S21. X. He, B. Yan, X. Zhang, Z. Liu, D. Bresser, J. Wang, R. Wang, X. Cao, Y. Su, H. Jia, C. P. Grey,
 H. Frielinghaus, D. G. Truhlar, M. Winter, J. Li, E. Paillard, *Nat. Commun.* 2018, *9*, 5320.
- S22. J. Xie, Z. Liang, Y.-C. Lu, Nat. Mater. 2020, 19, 1006–1011.