Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2022

Supporting Information

A low-concentration eutectic electrolyte for superior cycling ability of

aqueous zinc-ion capacitors

Xuejun Lu^a, Li Tao^a, Keqi Qu^a, Yue Zhang^a, Chang Liu,^{a,b} Robert Godin,^b Jian Liu^{a*}

 ^a School of Engineering, Faculty of Applied Science, University of British Columbia, Kelowna, BC V1V 1V7, Canada
^b Department of Chemistry, The University of British Columbia, 3247 University Way, Kelowna, BC, V1V 1V7, Canada.

* Corresponding author: Jian.liu@ubc.ca

Experimental Procedures

Electrolyte preparation:

All chemicals and reagents were analytical grade and used without further purification. LCEEs and aqueous $Zn(OTf)_2$ electrolytes were prepared according to the concentration unit of molality (mol kg⁻¹). The specific composition can be referred to in **Table S1**.

Cell assembly:

Commercial ASAC-30 (Alberta, Canada) carbon materials and Zn plate (~200 μ m in thickness) were used as cathodes and anodes of AZICs, respectively. For the cathodes, ASAC-30, acetylene black, and PTFE binder were mixed in a homogeneous slurry by adding alcohol with a weight ratio of 9:0.5:0.5, then the slurry was pressed on the Titanium (Ti) mesh. The prepared electrodes were vacuumed and dried at 120 °C for 6 h. Besides, glass fiber (GF/F, Whatman) was used as separators. For pouch cell fabrication, nickel foams were used as current collectors instead of Ti mesh.

Materials Characterizations:

Differential scanning calorimetry (DSC) thermogravimetric analysis (TGA) analyses were performed in a TA instrument DSC-Q1000 under a N_2 atmosphere. Raman spectra were recorded using a SENTERRA II model with an excitation wavelength of 532 nm. NMR measurements were carried out on an AVANCE III 400MHz equipment with BBO probe, samples were placed in NMR tubes and analyzed using a separated capillary tube with deuterated methanol (CD₃OD) as the external reference. Zygo Optical profilometer and scanning XPS spectra were obtained by Model number NV5000 5032 and PHI VersaProbe III Scanning XPS Microprobe, respectively.

Electrochemical Characterizations:

The ionic conductivity of electrolytes was tested at room temperature by two symmetric blocking stainless steel (SS) electrodes and calculated according to equation [1]:

$$\kappa = L/(R \cdot A)$$

[1]

where L and A are the thickness and effective contacting area between SS electrode and electrolyte, respectively, and R is the resistance obtained by electrochemical impedance spectroscopy (EIS) test. All electrochemical measurements including cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and EIS were performed using a VSP-3e Potentiostat. GCD cylcing ability was further tested in a NEWARE battery cycler (CT-4008T-5V50mA-164, Shenzhen, China). The gravimetric specific capacitance (C, F g⁻¹) based on GCD curves was calculated according to equation [2]:

 $C = (I \cdot \Delta t_1)/(m \cdot \Delta V)$ [2] where Δt_1 (s) is the discharge time, ΔV (V) is operation voltage (*e.g.*, 1.6 V) excluding the IR drop, *I* and *m* are applied current and active material loading on cathodes, respectively. The Coulombic efficiency (*CE*) was determined according to equation [3]: $CE = \Delta t_1/\Delta t_2$ [3] where Δt_2 (s) is the charge time. The mass energy density (*E*, Wh kg⁻¹) of AZICs were calculated by the equation [4]: $E = (I \cdot \Delta V \cdot \Delta t_1)/m$ [4] The power density (*P*, W kg⁻¹) was calculated as the equation [5]:

 $P = (E \cdot 3600) / \Delta t_1$ [5]

Ionic Models and Computational Methodology:

Quantum chemistry calculations were first performed to optimize molecular geometries of NMP molecules using the Gaussian 16 package [Gaussian-16] at the B3LYP/6-311+G(d,p) level of theory.^[1] The atomic partial charges on the NMP molecule were calculated using the ChelpG method at the same level of theory (the B3LYP hybrid functional and the 6-311+G(d,p) basis set). The atomistic force field parameters for all ions and molecules are described by the OPLS-AA format and are taken from previous work [oplsaa-ff].^[2] The cross-interaction parameters between different atom types are obtained from the Lorentz-Berthelot combination rule.

Atomistic simulations were performed using the GROMACS package with cubic periodic boundary conditions [gromacs].^[3] The detailed simulation system compositions are listed in Table S2. The equations for the motion of all atoms were integrated using a classic Verlet leapfrog integration algorithm with a time step of 1.0 fs. A cutoff radius of 1.6 nm was set for short-range van der Waals interactions and real-space electrostatic interactions. The particle-mesh Ewald (PME) summation method with an interpolation order of 5 and a Fourier grid spacing of 0.20 nm was employed to handle long-range electrostatic interactions in reciprocal space. All simulation systems were first energetically minimized using the steepest descent algorithm, and thereafter annealed gradually from 600 K to room temperature (300 K) within 10 ns. All annealed simulation systems were equilibrated in an isothermalisobaric (NPT) ensemble for 20 ns of physical time maintained using a Nosé-Hoover thermostat and a Parrinello-Rahman barostat with time coupling constants of 0.4 and 0.2 ps, respectively, to control the temperature at 300 K and the pressure at 1 atm. Atomistic simulations were further performed in a canonical ensemble (NVT) for 50 ns, and simulation trajectories were recorded at an interval of 100 fs for further structural and dynamical analysis.

	Molality (m)	Molar ratio		
Electrolytes		Salt	Solvent	
		Zn(OTf)₂	H ₂ O	NMP
Z ₂ W	2.0	1	27.8	
Z _{1.6} W-0.05NMP	1.6	1	27.8	1.4
Z _{1.3} W-0.1NMP	1.3	1	27.8	2.8
Z ₁ W-0.2NMP	1.0	1	27.8	5.6
Z _{0.8} W-0.3NMP	0.8	1	27.8	8.3

Table S1. Molar ratios of NMP versus H_2O in Z_2W electrolyte and LCEEs.



Figure S1. Ionic conductivity of Z_2W and LCEEs at -20 °C.



Figure S2. ¹⁹F NMR spectra of Z_2W and Z_1W -0.2NMP electrolytes.



Figure S3. Raman spectra of Z_2W electrolyte and LCEEs in the range of 0–4000 cm⁻¹ a) and b) 1400–1800 cm⁻¹.



Figure S4. FTIR spectra of pure H_2O , Z_2W electrolyte, and LCEEs in the range of 2500–4000 cm⁻¹.

Numbers of ions and molecules	Z ₂ W	Z ₁ W-0.2NMP	
Zn ²⁺	160	80	
OTf [_]	320	160	
H ₂ O	4448	2224	
NMP		448	
Total atoms	16064	15200	
Size of simulation box	(5.4279 nm) ³	(5.3843 nm) ³	

Table S2. Parameters	of MD	simulation b	oox.
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Figure S5. Atom's distance of Zn^{2+} among H_2O , NMP, and OTf^- in a) Z_2W and b) Z_1W -0.2NMP electrolytes.



Figure S6. a) Zn–F RDFs and CN of Z_2W and Z_1W -0.2NMP electrolytes. b) Zn–N RDFs and CN of Z_1W -0.2NMP electrolyte.



Figure S7. H-bonging structure between OTf^- and H_2O in both Z_2W and Z_1W -0.2NMP electrolytes.



Figure S8. H-bonging distance between H_2O and a) OTf^- in Z_2W or b) NMP in Z_1W -0.2NMP electrolyte.



Figure S9. Graphs of scan rate–dependent charge storage contributions from both capacitive and diffusion-controlled processes for Zn // AC coin cells with (a) Z_2W and (b) Z_1W -0.2NMP electrolytes.



Figure S10. CV and GCD profiles of aqueous $Zn(OTf)_2$ electrolytes. (a), (b) Z_1W ; (c), (d) Z_2W ; and (e), (f) $Z_{3.5}W$.



Figure S11. Price comparison of various salts and solvents as well as the corresponding electrolytes (sources from Sigma Aldrich USA in June, 2022).



Figure S12. Images of aqueous $Zn(OTf)_2$ and LCEE electrolytes at various concentrations. All samples have been placed at 20 °C and -40 °C.



Figure S13. CV and GCD profiles of LCEE electrolytes. (a), (b) $Z_{1.6}W$ -0.05NMP; (c), (d) $Z_{1.3}W$ -0.1NMP; (e), (f) Z_1W -0.2NMP; and (g), (h) $Z_{0.8}W$ -0.3NMP.



Figure S14. Plots of capacitance *vs.* current densities for (a) aqueous $Zn(OTf)_2$ and (b) LCEE electrolytes, respectively.



Figure S15. (a) CV and (b) GCD profiles of Z_2W and Z_1W -0.2NMP electrolytes operated at -20 °C.



Figure S16. (a) CV and (b) GCD profiles of Z_2W and Z_1W -0.2NMP electrolytes operated at 60 °C.



Figure S17. (a) CV and (b) GCD profiles of Z_1W -0.2NMP electrolytes operated at -40 °C.



Figure S18. Ragone plots of Z_2W , Z_1W -0.2NMP electrolytes and examples from refs below.



Figure S19. Cycling performance of Z_1W -0.2NMP electrolyte in Zn // Zn symmetric cells at the current density of 5 mA cm⁻² with 1 mAh cm⁻².



Figure S20. SEM images of cycled Zn anodes at two positions in Z_2W and Z_1W -0.2NMP electrolytes, respectively.



Figure S21. Cycling stability of $Z_{3.5}W$, $Z_{1.3}W$ -0.1NMP, and $Z_{0.8}W$ -0.3NMP in Zn // AC coin cells at 4 A g⁻¹ for 50,000 cycles.



Figure S22. Full XPS spectra of Zn anodes cycled in Z_2W and Z_1W -0.2NMP electrolytes.



Figure S23. Nyquist plots of Z_1W -0.2NMP electrolyte in coin cells and various sizes of pouch cells.

Table S3. Summary of various electrolytes used in Zn-ion capacitors.

Electrolytes	Cathodes	Capacitance	Cycles number	Capacitance	Ref.
		(F g ⁻¹)	(n)	Retention	
			50,000	100.0%	
Z ₁ W-0.2NMP	ASAC-30	275.3	(4 A g ⁻¹)	100.0%	This weath
		(0.5 A g ⁻¹)	100,000	05.0%	
			(8 A g ⁻¹)	95.0%	
2 m	ASAC 20	197.0	Fail	Fail	This work
Zn(OTf) ₂ -H ₂ O	ASAC-SU	(0.5 A g ⁻¹)		Fall	This work
3.5 m		246.3	50,000	CO 0%	This work
Zn(OTf) ₂ -H ₂ O	ASAC-30	(0.5 A g ⁻¹)	(4 A g ⁻¹)	69.0%	This work
3 M	aMEGO	~210.0	80,000	02.0%	[4]
Zn(OTf) ₂ -H ₂ O		(0.1 A g ⁻¹)	(8 A g ⁻¹)	93.0%	[4]
7.5 m	SAC	319.4	100,000	OF 19/	[5]
ZnCl ₂ hydrogel		(0.5 A g ⁻¹)	(5 A g ⁻¹)	95.1%	[ວ]
3 M	PC-800	340.7	30,000	00/29/	[6]
Zn(ClO ₄) ₂ -H ₂ O		(0.1 A g ⁻¹)	(20 A g ⁻¹)	99/2%	[0]
1M	TiN	489.8	6700 h	84.6%	[7]
ZnSO ₄ -H ₂ O		(0.2 A g ⁻¹)	(0.2 A g ⁻¹)		[7]
1 M					
Zn(OTf) ₂ in		170.0	20,000		
(DME)/1,3-	HSC	$(0.1 \wedge a^{-1})$	$(2 \land a^{-1})$	91.0%	[8]
dioxolane		(0.1 A g -)	(∠Ağ ⁻)		
(DOL) (1:1 v/v)					

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