Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Regulating solvation structure and interfacial chemistry via multifunctional acetylurea for highly reversible neutral zinc-manganese flow batteries

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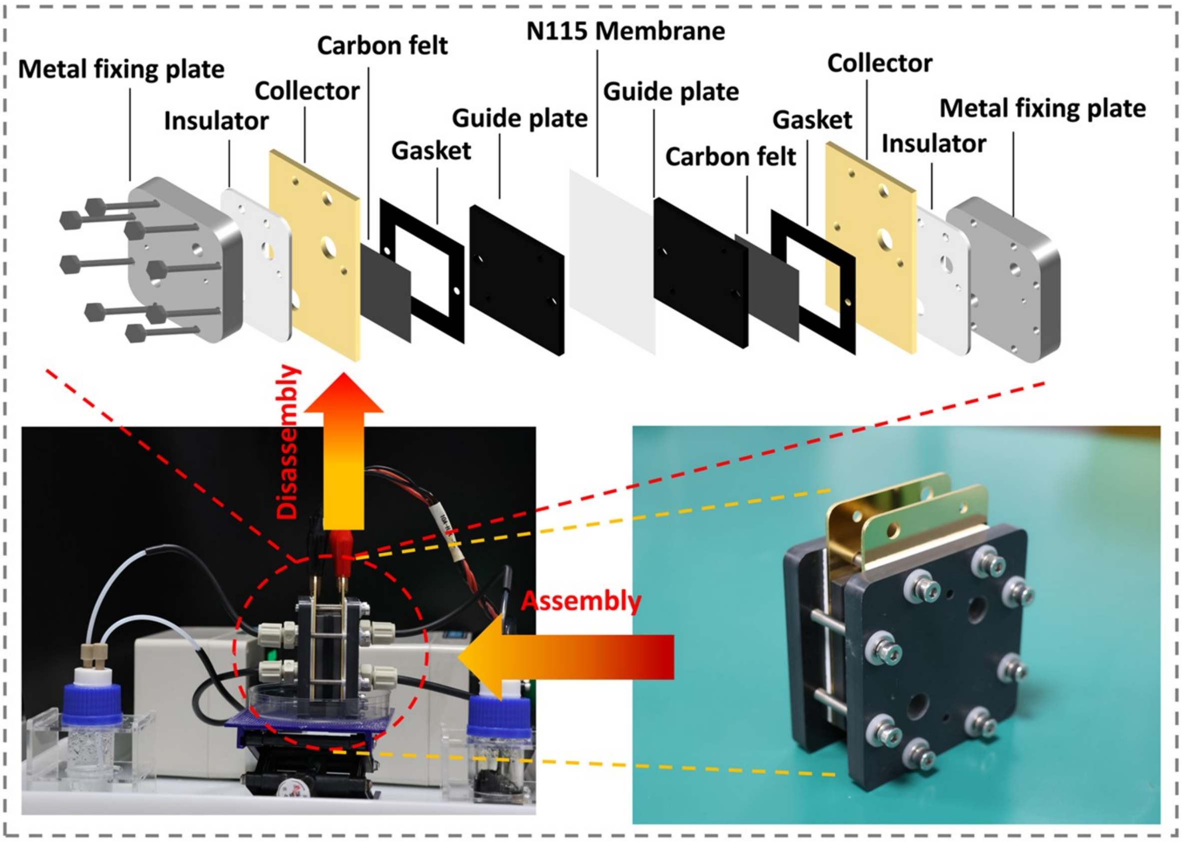

Fig. S1 Illustration of the disassembly and assembly of a typical ZMFB.

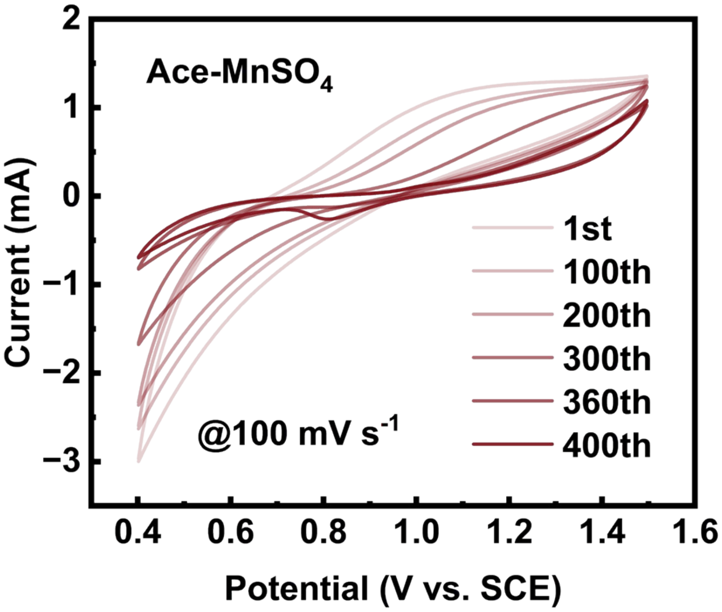

Fig. S2 Long-term stability of Ace over 400 cycles.

Fig. S3 Optical images of electrolyte solutions with and without Ace.

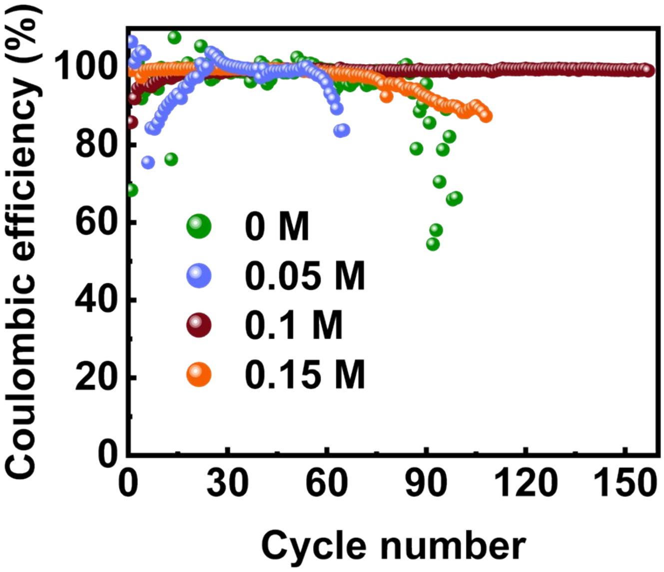

Fig. S4 The influence of different concentrations of Ace on cycling performance.

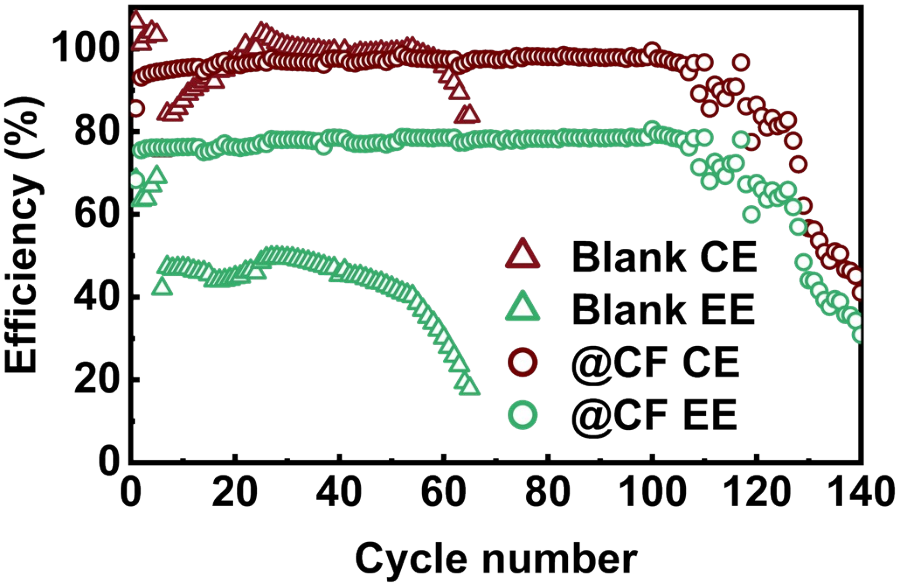

Fig. S5 Effect of Ace-pretreated carbon felt on cycling performance.

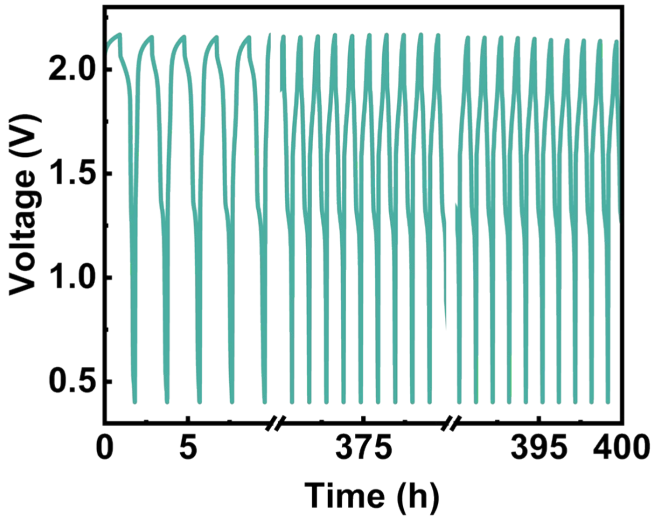

Fig. S6 Long-term cycling stability of the Ace-based ZMFB at 20 mA cm^{-2}.

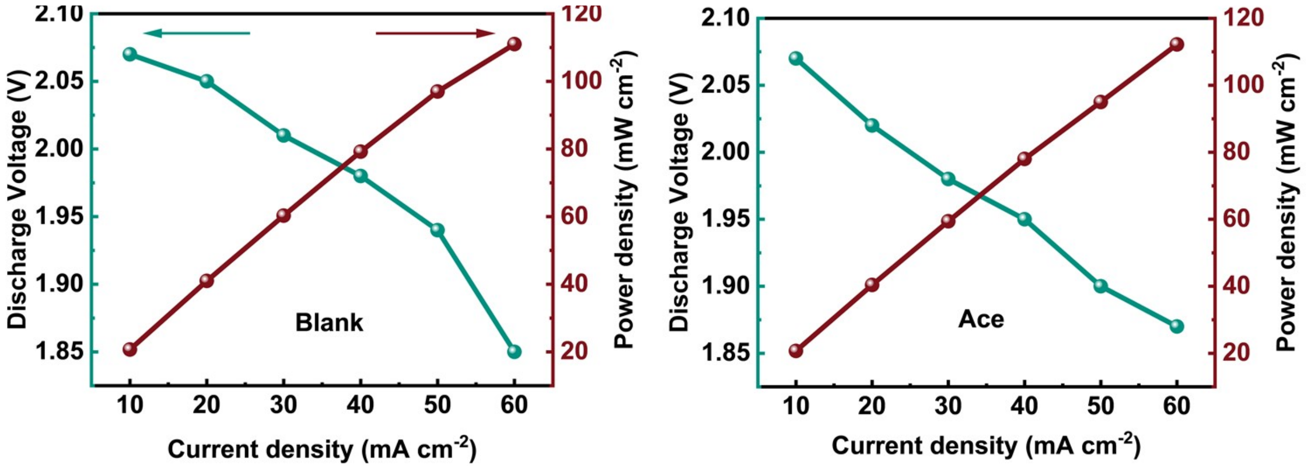

Fig. S7 Power density plots of the ZMFB systems with and without the Ace additive.

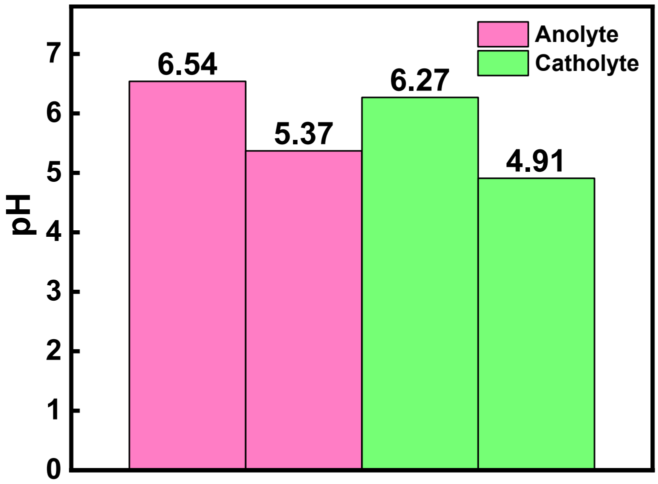

Fig. S8 pH variation of the electrolyte before and after circulation.

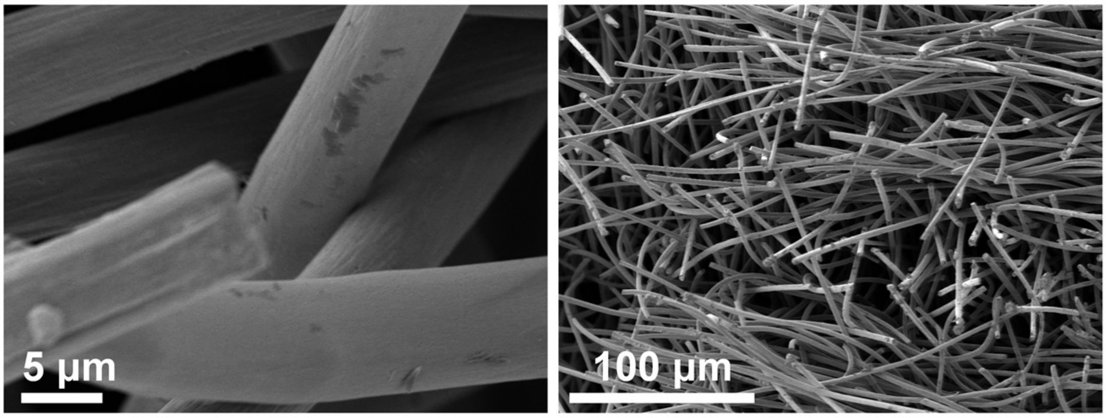

Fig. S9 SEM image of pristine carbon felt.

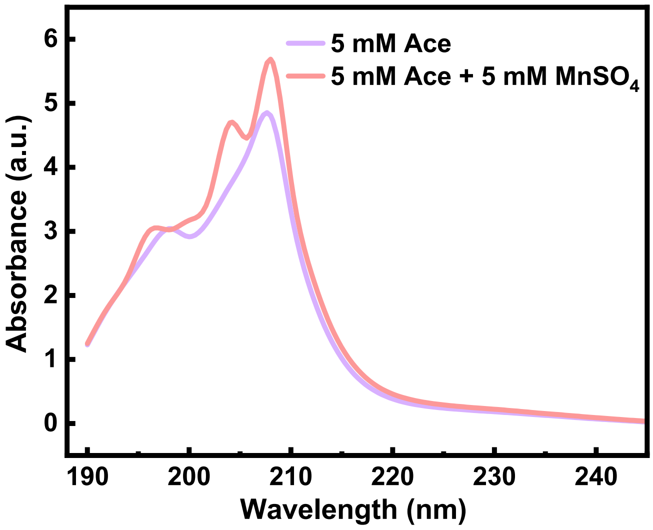

Fig. S10 UV-vis absorption spectra of Ace and Ace/$MnSO_4$ aqueous solutions.

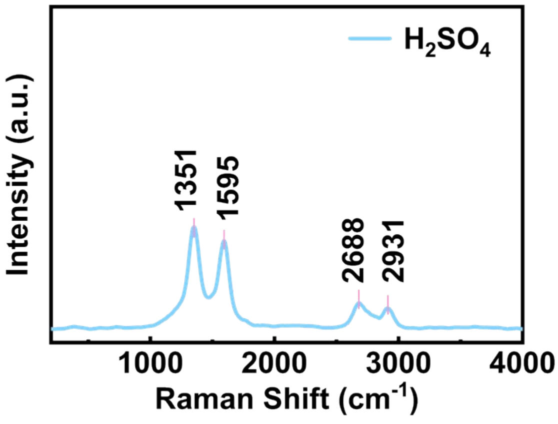

Fig. S11 Raman spectrum of carbon felt treated only with H_2SO_4.

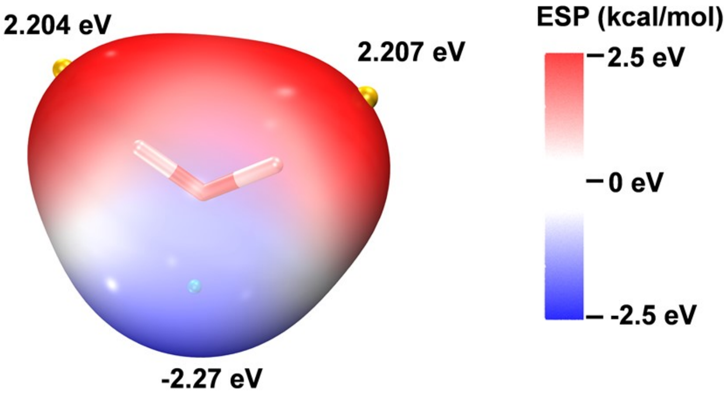

Fig. S12 Electrostatic potential map of a water molecule.

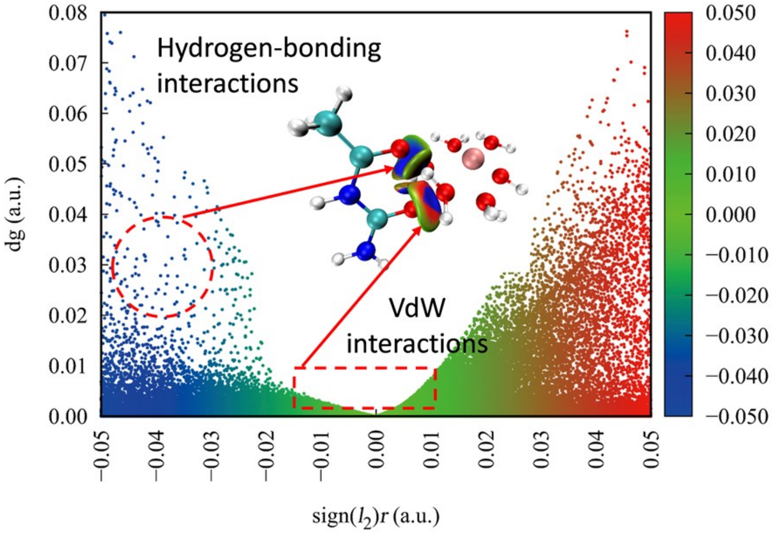

Fig. S13 IGMH analysis of Ace and the solvation structure of manganese ions.

Table S1 Comparison of different ZMFBs in this work and previous reports.

Systems	Areal capacity (mAh cm^{-2})	Current density (mA cm^{-2})	Coulombic efficiency (%)	Cycle number	Accumulated Capacity (mAh)	Refs.

0.5 M $MnSO_4$ +2 M KCl + 0.1 M Ace; 0.5 M $Zn(Ac)_2$ + 2 M KCl	20	40	95.7	70	1339.8	This work
	10	20	99.1	380	3765.8	
0.5 M $Mn(Ac)_2$ + 0.5 M $ZnCl_2$ + 2 M KCl	10	40	96.3	/	/	[1] *Energy & Environmental Science*
1.5 M $Mn(Ac)_2$ + 1.5 M $ZnCl_2$ + 3 M KCl	20	40	95	30	570.0	
1 M H_2SO_4 + 1 M $MnSO_4$ + 1 M Na_2SO_4 + 50 mM $VOSO_4$; 0.5 M $Zn(Ac)_2$ + 2 M NaAc + 2 M HAc	10	20	98.3	90	884.7	[2] *ACS Sustainable Chemistry & Engineering*
	20	20	99.0	60	1188.0	
4 M $ZnCl_2$ + 4 M $MnCl_2$ +1 M KCl + 1 M Gly	10	20	91.1	20	182.2	[3] *Chemical Engineering Journal*
0.5 M EDTA-Mn + 3 M NaCl; 0.5 M $ZnCl_2$ + 3 M NaCl	/	20	98	300	/	[4] *Journal of Power Sources*
1 M EDTA-Mn	3.3	20	95	100	313.5	
0.5 M $ZnCl_2$ + 0.5 M $Mn(Ac)_2$ + 2 M KCl + 1.75 M HAc	2	50	95	/	/	[5] *Energy Storage Materials*
0.5 M $Mn(Ac)_2$ + 0.5 M $Zn(Ac)_2$ + 2 M KCl	15	40	/	180	2766.7	[6] *Small*

Table S2 Calculated formation energies for the various models.

Model	**E_f (eV)**
$[Mn(H_2O)_6]^{2+}$	-14.50
Ace-$[Mn(H_2O)_5]^{2+}$	**-16.33**
2Ace-$[Mn(H_2O)_4]^{2+}$	-9.30
3Ace-$[Mn(H_2O)_3]^{2+}$	-3.76
4Ace-$[Mn(H_2O)_2]^{2+}$	Non-convergence
5Ace-$[Mn(H_2O)_1]^{2+}$	Non-convergence
6Ace-Mn^{2+}	Non-convergence

Cost calculation

The preliminary cost assessment focuses on the electrolyte compositions of both electrodes. The catholyte comprises an aqueous solution of 0.5 M $MnSO_4{\cdot}H_2O$ and 2 M KCl, with 0.1 M Ace evaluated as an additive. The anolyte consists of 0.5 M $Zn(Ac)_2$ and 2 M KCl. The unit prices of all individual electrolyte components are detailed in Table S3.

Table S3 Estimated cost of the electrolyte solution.

Chemical	**Price [US$ g^{-1}]***	**Molar mass (g mol^{-1})**
$MnSO_4{\cdot}H_2O$	0.00056	169.02
$Zn(Ac)_2$	0.00030	183.48

KCl	0.00026	74.55
Ace	0.00025	102.09

* Prices quoted from Sigma-Aldrich Corporation.

The overall chemical cost for both the anolyte and catholyte is derived from the summation of their individual constituent prices.

Cost of (catholyte) = [$5.6 \times 10^{-4} \times 169.02\ \text{g mol}^{-1} \times 0.5\ \text{mol L}^{-1} + 2.6 \times 10^{-4} \times 74.55\ \text{g mol}^{-1} \times 2\ \text{mol L}^{-1} + 2.5 \times 10^{-4} \times 102.09\ \text{g mol}^{-1} \times 0.1\ \text{mol L}^{-1}$] = 0.0886 $

Cost of (anolyte) = [$3.0 \times 10^{-4} \times 183.48\ \text{g mol}^{-1} \times 0.5\ \text{mol L}^{-1} + 2.6 \times 10^{-4} \times 74.55\ \text{g mol}^{-1} \times 2\ \text{mol L}^{-1}$] = 0.0663 $

C_e=0.0886 $ + 0.0663 $ =0.1549 $

The battery system employs a Nafion 115 membrane with a unit price of 500 $/m². The effective membrane area was approximately the same as that of the electrode frame, with dimensions of 3 cm × 3 cm, corresponding to 0.0009 m². Accordingly, the membrane cost for a single cell was estimated to be C_m=0.000 9 m² × 500 $/m² = 0.4500 $

The total cost $C_t = C_e + C_m$ = 0.1549 $ + 0.4500$ = 0.6049 $

The single-cell capacity of the ZMFB in this study (C_s) is 0.09 Ah. The total energy delivered by a single cell was calculated according to the following equation:

$$E_{st} = \text{OCV} \times C_s = 1.5 \text{ X } 0.09 = 0.135 \text{ Wh}$$

The total system cost (C_{st}) was then calculated according to the following equation:

$$C_{st} = \frac{C_t}{E_{st}} = \frac{0.4531}{0.1350} = 3.356 \ \$/\text{Wh}$$

where C_e, C_m, E_{st}, C_s denote the total electrolyte cost, membrane cost, single-cell energy, and single-cell capacity, respectively.

It should be noted that this simplified estimate excludes stack hardware, current collectors, flow-field plates, frames, gaskets, electrolyte tanks, pumps, tubing, power electronics, manufacturing, assembly, maintenance, and lifetime-dependent replacement costs. Therefore, a complete techno-economic analysis is required before assessing the practical system-level cost of this chemistry.

The coulombic efficiency (CE), voltage efficiency (VE), and energy efficiency (EE) were calculated using the following equations:

$$\text{CE} = \frac{C_{\textbf{discharge}}}{C_{\textbf{charge}}} \times 100\%$$

$$\text{VE} = \frac{V_{\textbf{discharge}}}{V_{\textbf{charge}}} \times 100\%$$

$$\text{EE} = \text{CE} \times \text{VE}$$

where $C_{discharge}$ refers to the discharge capacity of the battery during cycling, while C_{charge} denotes the charging capacity. Additionally, $V_{discharge}$ represents the discharge voltage of the battery, and V_{charge} signifies the charging voltage.

Reference

[1] C. Xie, T. Li, C. Deng, Y. Song, H. Zhang, X. Li, Energy & Environ. Sci. 2020, 13, 135.

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