Supplementary Information (SI) for Soft Matter.

Supplementary Information

Ca^{2+}/Zn^{2+} Alginate Hydrogel Electrolyte for High-Performance Zinc-Ion Batteries

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S1. Materials

Sodium alginate (SA, AR, > 99 %) were purchased from Aladdin Chemical Reagent Co., Ltd. $CaCl_2 \cdot 2H_2O$ (AR, > 99 %), $ZnSO_4 \cdot 7H_2O$(AR, > 99 %) was purchased from Macklin Chemical Reagent Co., Ltd..

S2. Preparation of hydrogel electrolytes

Firstly, 1 g of SA (sodium alginate) was homogeneously mixed with 49 mL of H_2O at room temperature under constant stirring. An appropriate amount of the precursor solution was then drawn using a syringe and injected into the mold, followed by standing until a uniform liquid level was achieved. Subsequently, 1 wt% $CaCl_2$ solution and 2M $ZnSO_4$ were sequentially added to prepare SCa (calcium-crosslinked) and SZn (zinc-crosslinked) hydrogels, respectively. The as-prepared SCa and SZn hydrogels were then immersed in 2M $ZnSO_4$ solution for 24 h to undergo secondary crosslinking and ion exchange processes, ultimately yielding SZn and SCZ (calcium-zinc bimetallic crosslinked) hydrogel electrolytes.

S3. Characterization

The surface morphologies of the hydrogel and Zn anode were determined using a scanning electron microscope (SEM, QUANTA 250 FEG, 30 kV). The hydrogel sample was analyzed by Fourier transform infrared spectroscopy (FTIR, Bruker Vertex-70). The crystal structure of the Zn anode was characterized using an X-ray diffractometer (XRD, SmartLab 9KW).

The tensile strength of the hydrogel was measured using a universal mechanical testing machine.

All electrochemical performance tests were conducted at room temperature. CR2032-type coin cells (Zn//Zn, Zn//Cu, and Zn//MnO_2) were assembled in an ambient atmosphere using glass fiber as the separator and 90 μL of 2M $ZnSO_4$ solution with SZn and SCZ as electrolytes. All cells were allowed to rest for 6 h after assembly. The cycling performance of Zn//Zn cells was evaluated, while the coulombic efficiency of Zn//Cu cells was tested on a Neware battery testing system. Galvanostatic charge-discharge tests (CT-4008T) were performed for Zn//MnO_2 cells.

Cyclic voltammetry (CV), linear sweep voltammetry (LSV), and electrochemical impedance spectroscopy (EIS) measurements (frequency range: 10^{-1}~10^{5} Hz) were carried out on an electrochemical workstation (EmStat 4S HR, PalmSens, Netherlands).

S4. Water content and porosity

The water content (W_c) of the SCZ hydrogel was determined using a simple "drying method." To ensure accuracy, three parallel samples were vacuum-dried at 60 °C for 24 h. The calculation formula is as follows:

$$W_c = \frac{M_0 - M_s}{M_0} \cdot 100\ \%$$

where M_0 is the initial mass of the sample and M_s is the mass after drying.

The water content values for the three samples were 63.46%, 64.44%, and 64.13%, respectively. Its average value is 64.01 %.

Porosity was measured using the liquid displacement method. Three parallel samples were freeze-dried for 12 h. The calculation formula is as follows:

$$Porosity = \frac{W_f - W_0}{\rho V_0} \cdot 100\ \%$$

where W_f is the final mass of the sample, W_0 is the initial mass, V_0 is the volume of the sample, and ρ is the density of ethanol at room temperature (0.789 g/cm³).

The porosity values for the three samples were 67.43%, 67.63%, and 68.28%, respectively. Its average value is 67.78 %.

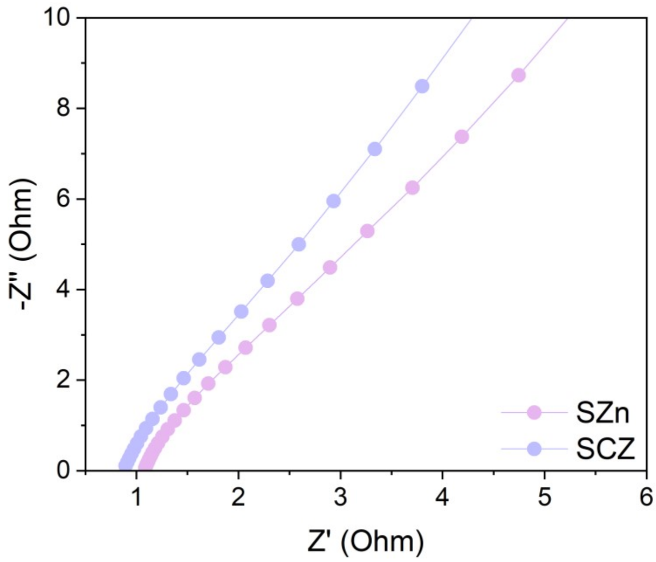

Figure S1. The electrochemical impedance spectra (EIS) of SZn and SCZ were measured in the frequency range of 10^{-1}~10^{5} Hz under open-circuit potential conditions.

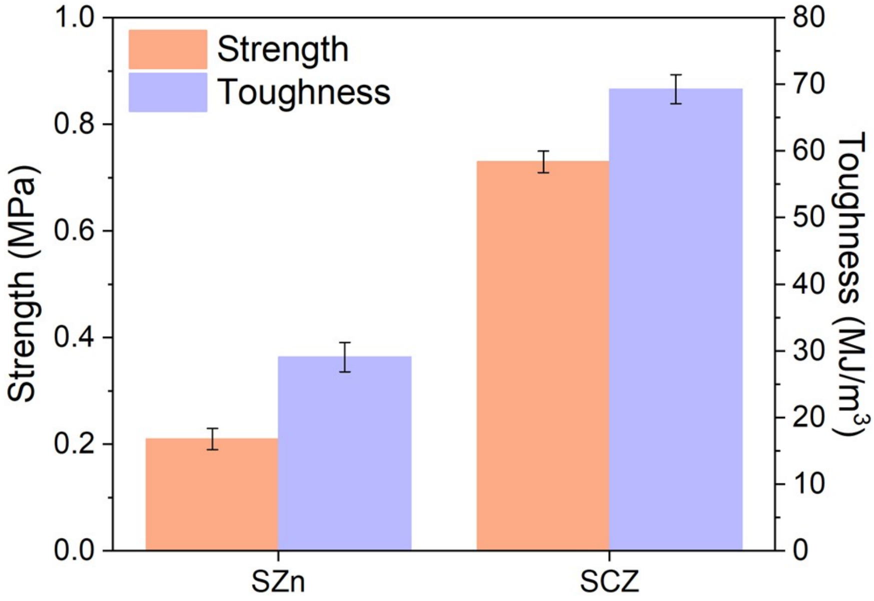

Figure S2. The strength and toughness of SZn and SCZ hydrogels.

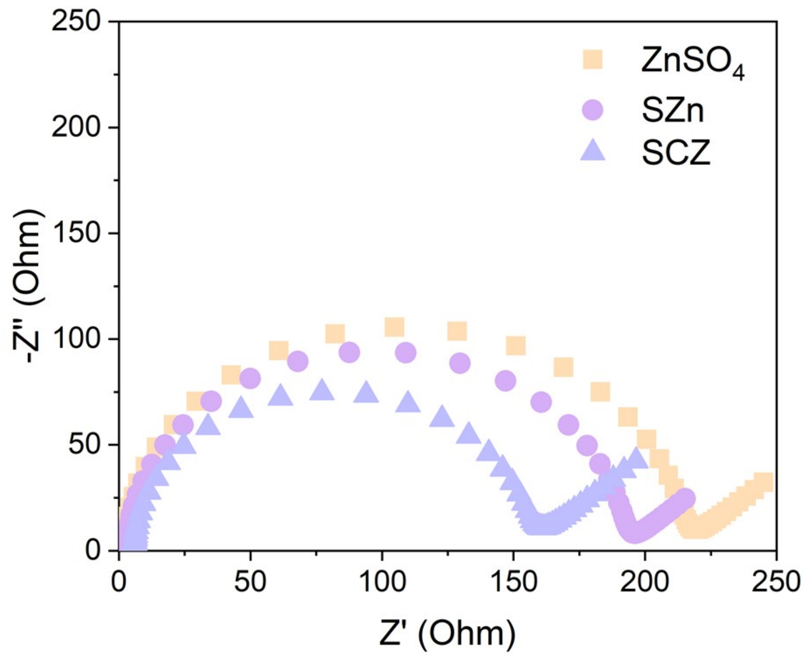

Figure S3. The EIS of Zn//Zn symmetric cells assembled with $ZnSO_4$, SZn, and SCZ electrolytes were measured in the frequency range of 10^{-1}~10^5 Hz under open-circuit potential (OCP) conditions.

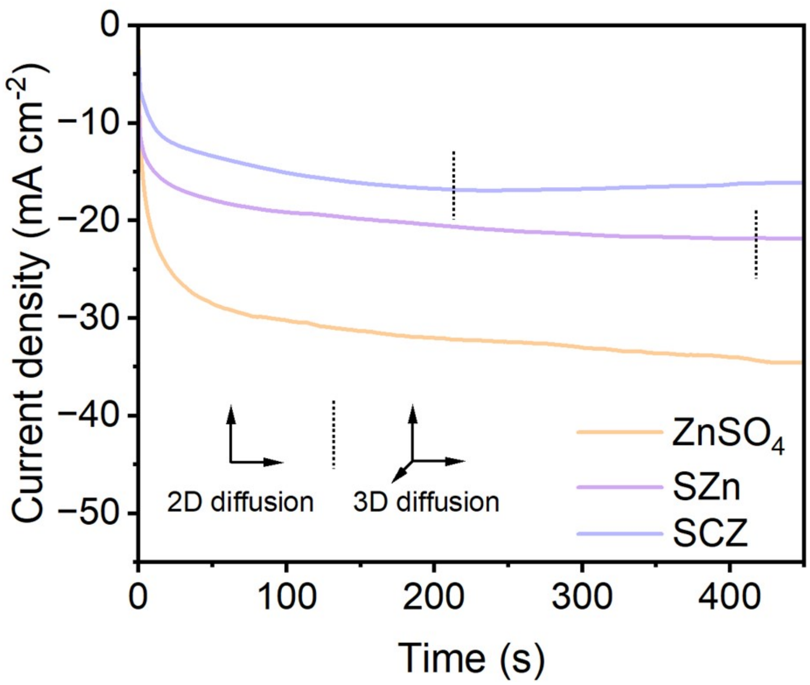

Figure S4. Chronoamperometry curves of the Zn//Zn cell at a constant voltage of -150 mV.

Table S1 The performance comparison between SCZ electrolyte and reported hydrogel electrolytes.

Types of hydrogels	σ （kPa）	ε （%）	Conductivity （mS/cm）	Zn//Zn Cycle life（h）	*Reference*
SCZ	730	186	18.0	1100 (1 mA cm^{-2})	This work
PAM-SL-QCS	81	1700	28.0	520 (0.5 mA cm^{-2})	Ref. 1
PI2	280	362	12.5	800 (0.2 mA cm^{-2})	Ref. 2
GP30HE	2400	370	12.6	1000 (0.5 mA cm^{-2})	Ref. 3
DN-PC100-1wt%	150	1080	17.4	600 (1 mA cm^{-2})	Ref. 4
PSAZn	21	620	59.0	800 (1 mA cm^{-2})	Ref. 5
CMC/GO	1380	70	20.5	800 (1 mA cm^{-2})	Ref. 6

References

1. Y. Wu, S. Liao, Z. Zeng and J. Qu, *European Polymer Journal*, 2025, **238**.
2. Y. Chen, M. Zhu, C. Li, H. Wang, D. Chen, H. Wu, Z. Huang, Y. Wang, Y. Fan, Z. Bai, S. Chen, Y. Tang and Y. Zhang, *Advanced Functional Materials*, 2025, **35**.
3. Q. Xie, H. Zhang, L. Wang, R. Dong, W. Xie, M. Asraful Alam, J. Xu and W. Xiong, *Journal of Colloid and Interface Science*, 2025, **697**.
4. A. Somteds, P. Tayraukham, P. Pipattanachaiyanan, W. Kao-ian, S. Wannapaiboon, S. Loiha, N. Sukpirom, M. Suttipong, J. Guo, S. Kheawhom and J. Unruangsri, *ACS Sustainable Chemistry & Engineering*, 2025, **13**, 9974-9986.
5. Y. Xu, B. Lan, Y. Cheng, L. Shi, J. Sun, S. Sun and R. Wang, *Journal of Materials Chemistry A*, 2024, **12**, 13191-13202.
6. X. Li, Y. Li, Y. Jiang, D. Wang and F. Ran, *Green Energy & Environment*, 2025, **10**, 537-550.