

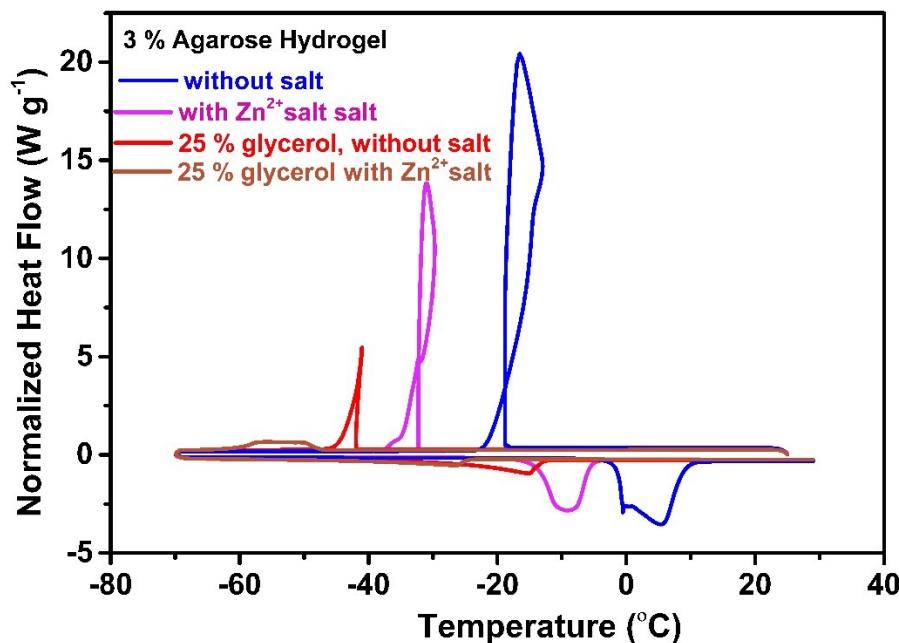
## Safe and Stable Zn-Lignin battery with Bio-polymer based Hydrogel Electrolyte

Ujwala Ail<sup>a\*</sup>, Jakob Backe<sup>b</sup>, Zia Ullah Khan<sup>a</sup>, Rui Shu<sup>a</sup>, Jaywant Phopase<sup>a</sup>, Magnus Berggren<sup>c</sup> and Reverant Crispin<sup>a,c\*</sup>.

*a.* Laboratory of Organic Electronics (LOE), Department of Technology and Natural Sciences (ITN), Linköping University, SE-601 74 Norrköping, Sweden;  
E-mail: reverant.crispin@liu.se, ujwala.ail@liu.se

*b.* Ligna Energy AB, Källvindsgatan 5, 60240 Norrköping, Sweden

*c.* Wallenberg Wood Science Center, Department of Science and Technology (ITN), Linköping University, SE-60174 Norrköping, Sweden



**Fig. S1** DSC data showing the effect of salt and glycerol on the 3 % agarose hydrogel with both cooling and heating cycle information.

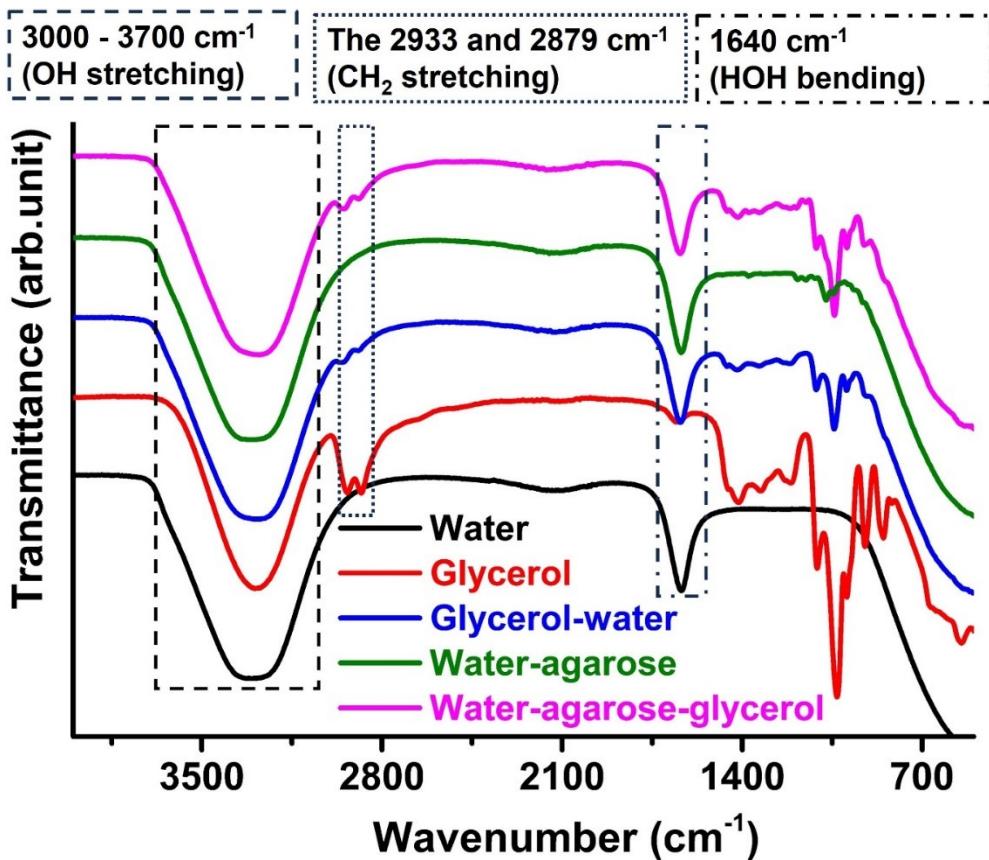


Fig. S2 FTIR spectra showing different band regions of the glycerol, water, agarose and their mixtures.

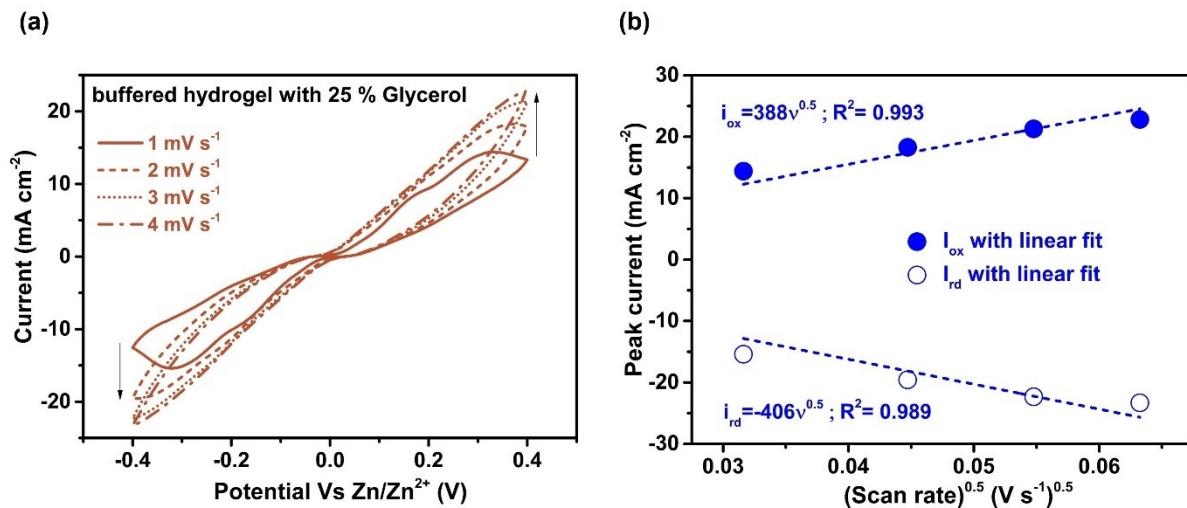


Fig. S3 (a) CV of buffered hydrogel electrolyte with 1 M  $\text{Zn}^{2+}$  containing 25 % glycerol at different scan rates, (b) peak current vs square root of scan rate indicating the diffusion-controlled process.

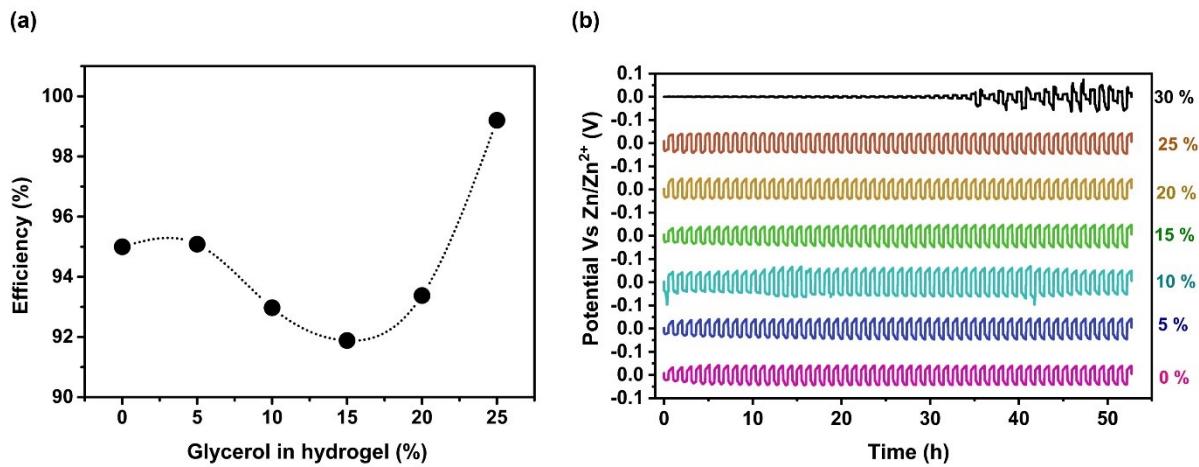


Fig. S4 (a) Charge efficiency obtained from CV of buffered hydrogel electrolyte with 1 M Zn<sup>2+</sup> containing different amounts of glycerol (b) Galvanostatic cycling of Zn plating and stripping with buffered hydrogel electrolyte with 1 M Zn<sup>2+</sup> containing different amounts of glycerol.

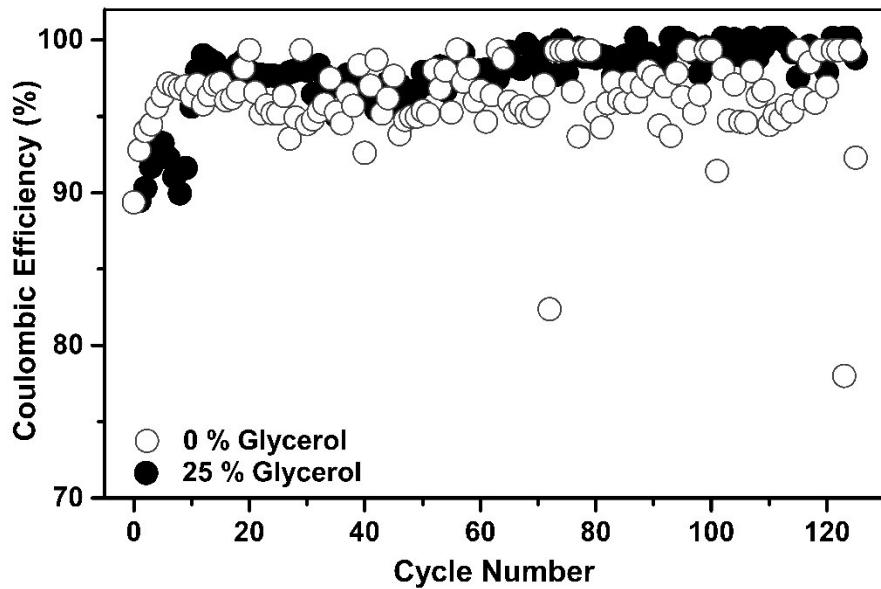


Fig. S5 Coulombic efficiencies evaluation of Zn||Ti asymmetrical cells using galvanostatic cycling at 1 mA cm<sup>-2</sup> and capacity of 0.5 mAh cm<sup>-2</sup> using 3 % agarose buffered hydrogel electrolyte with 0 and 25 % glycerol.

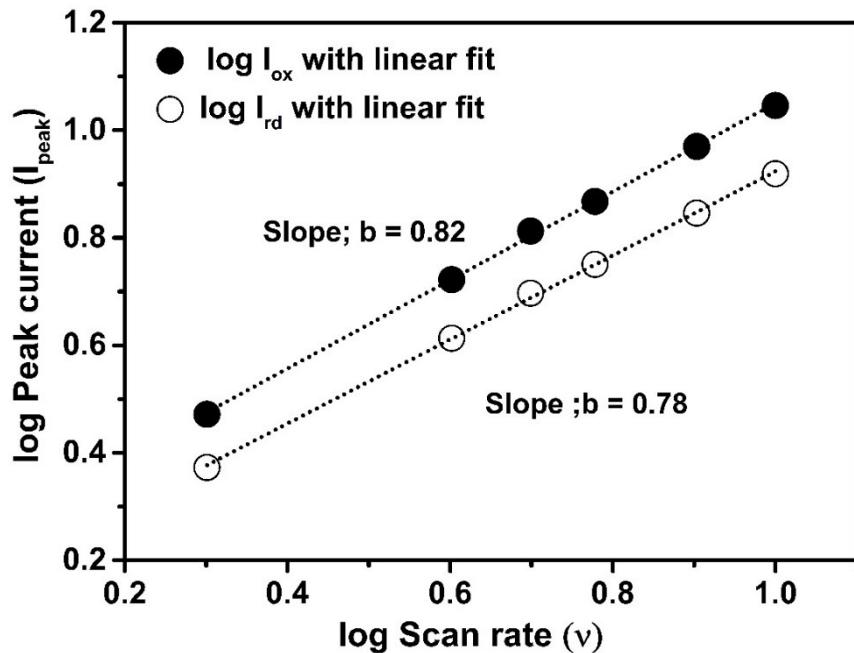


Fig. S6 Plots of peak current (mA) vs scan rate ( $\text{mV s}^{-1}$ ) in logarithmic scale to obtain the b-values according to,  $i = av^b$ ; where  $i$  is the peak current,  $v$  is the scan rate,  $a$  and  $b$  are constants.

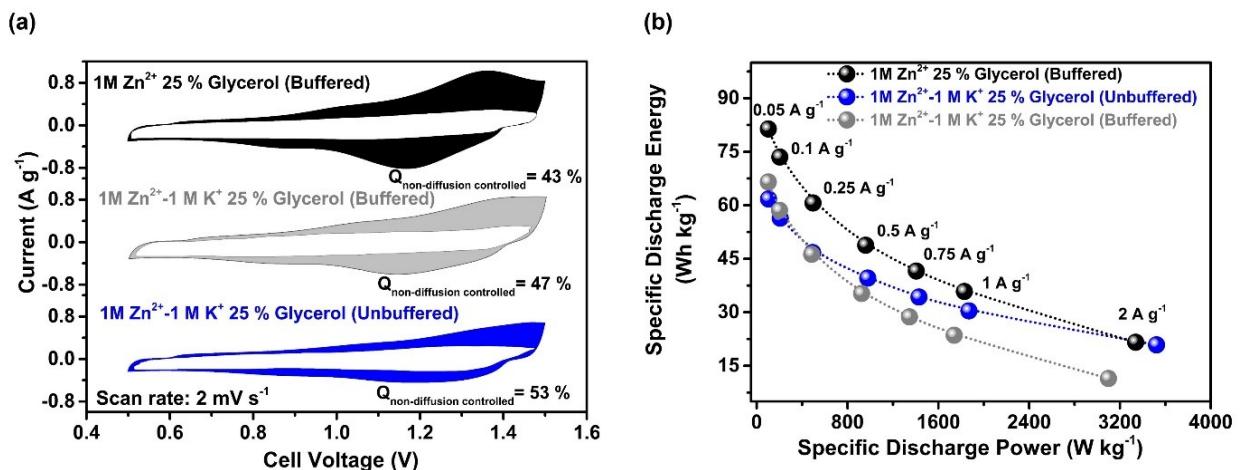


Fig. S7 (a) Comparison of the CV at  $2 \text{ mV s}^{-1}$  with contribution from the diffusion controlled and non-diffusion-controlled charge storage processes, (b) Ragone plot comparison of the cells with Zn anode, LC/C composite cathode, and the electrolyte: buffered 3 % agarose hydrogel containing 25 % glycerol with only  $1\text{M Zn}^{2+}$  (black data), with  $1\text{M Zn}^{2+}$  and  $1\text{M K}^{+}$  (gray data), unbuffered 3 % agarose hydrogel containing 25 % glycerol with  $1\text{M Zn}^{2+}$  and  $1\text{M K}^{+}$  (blue data). Here the specific energy and specific power are presented by considering the mass of LC only and mass of carbon and Zn foil are not included.

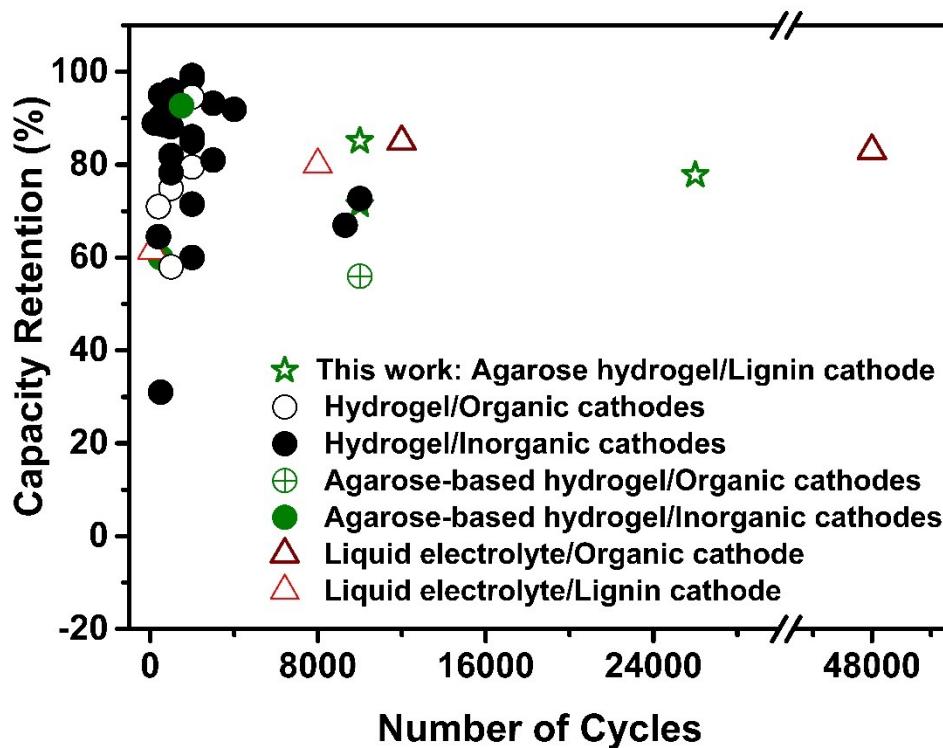


Fig. S8 The comparison of the Zn-ion device with hydrogel- based electrolytes except for the data presented by triangles. The data presented by the black filled circles are for the inorganic based cathode,<sup>1, 2, 3-22</sup> whereas black open circles are for the organic cathode materials.<sup>23-27</sup> The data presented in green open circle with + correspond to the agarose- based hydrogel with organic cathode<sup>28</sup> and the green closed circles present the agarose- based hydrogels with inorganic cathodes.<sup>29,30</sup> The data shown in red open triangle is for lignin-based cathode in liquid electrolyte<sup>31,32</sup> and brown open triangle is poly catechol- based cathode in liquid electrolyte.<sup>33</sup> The data from the present study (lignocatechol cathode and agarose-based hydrogel electrolyte) is presented in green stars. It is important to note that the cyclic performances presented in the plot are not performed at the same charge/discharge rates rather they vary from  $0.1 \text{ A g}^{-1}$  to  $10 \text{ A g}^{-1}$  and majority of the cathode materials studied in the hydrogel electrolytes are based on  $\text{V}_2\text{O}_5$ ,  $\text{MnO}_2$  systems and there are not many reports on the organic based-cathodes in the hydrogel electrolytes for Zn-ion energy storage system.

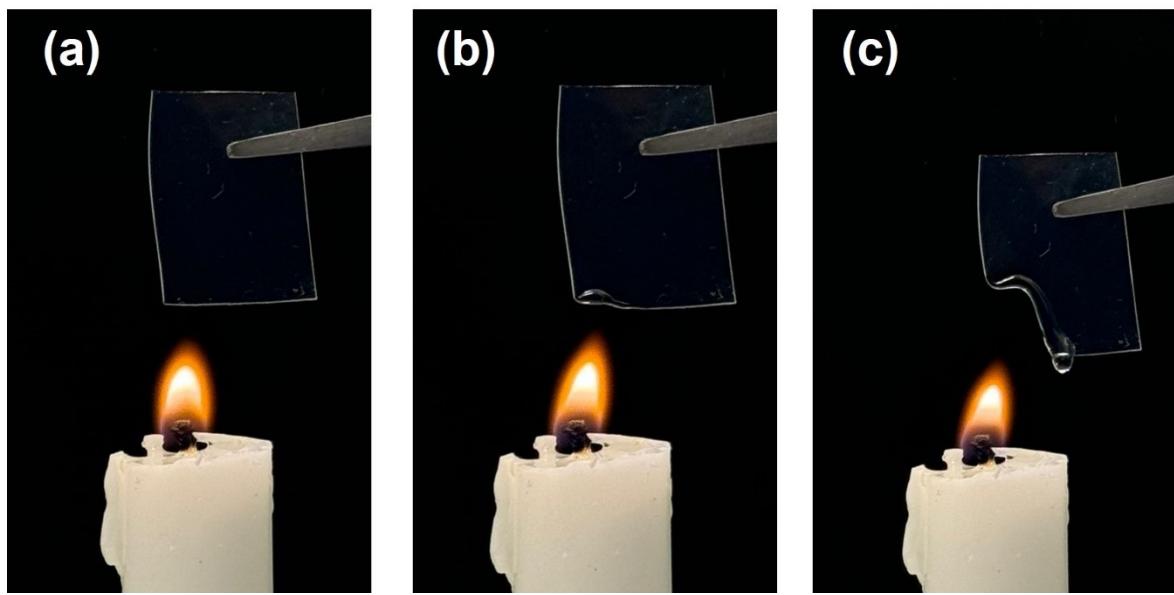


Fig. S9 Flame test of the hydrogel electrolyte, showing the softening of the hydrogel. Absence of visible flame during burning indicates the non-flammability of the decomposition products.<sup>34</sup>

Some of the literatures indicating the sustainability of the components used in Zn-Lignin study are presented in the references. <sup>35-41</sup>

## References

1. Z. Zheng, S. Yan, Y. Zhang, X. Zhang, J. Zhou, J. Ye, Y. Zhu, *Chem. Eng. J.* 2023, **475**, 146314.
2. J. Wang, Y. Huang, B. Liu, Z. Li, J. Zhang, G. Yang, P. Hiralal, S. Jin, H. Zhou, *Energy. Storage Mater.* 2021, **41**, 599.
3. X. Yue, Q. Wang, K. Ao, J. Shi, X. Zhang, H. Zhao, K. Uyanga, Y. Yang, W. A. Daoud, *J. Power Sources*, 2023, **557**, 232553.
4. L. Xu, T. Meng, X. Zheng, T. Li, A. H. Brozena, Y. Mao, Q. Zhang, B. C. Clifford, J. Rao, L. Hu, *Adv. Funct. Mater.*, 2023, **33**, 2302098.
5. Q. Zhang, C. Li, Q. Li, Z. Pan, J. Sun, Z. Zhou, B. He, P. Man, L. Xie, L. Kang, X. Wang, J. Yang, T. Zhang, P. P. Shum, Q. Li, Y. Yao, L. Wei, *Nano Lett.* 2019, **19**, 4035.
6. M. Chen, J. Chen, W. Zhou, X. Han, Y. Yao, C-P. Wong, *Adv. Mater.*, 2021, **33**, 2007559.

7. J. Guo, Y. Wang, S. Li, Y. Meng, Y. Qin, L. Jiang, H. Huang, L. Shen, *J. Alloys Compd.*, 2023, **967** 171708.
8. H. Lu, J. Hu, X. Wei, K. Zhang, X. Xiao, J. Zhao, Q. Hu, J. Yu, G. Zhou, B. Xu, *Nat Commun* 2023, **14**, 4435.
9. Z. Zheng, H. Cao, W. Shi, C. She, X. Zhou, L. Liu, Y. Zhu, *Polymers* 2023, **15**, 212.
10. B. Zhang, L. Qin, Y. Fang, Y. Chai, X. Xie, B. Lu, S. Liang, J. Zhou, *Sci. Bull.*, 2022, **67**, 955.
11. Q. Han, X. Chi, S. Zhang, Y. Liu, B. Zhou, J. Yang, Y. Liu, *J. Mater. Chem. A*, 2018, **6**, 23046.
12. G. Cao, L. Zhao, X. Ji, Y. Peng, M. Yu, X. Wang, X. Li, F. Ran, *Small* 2023, **19**, e2207610.
13. Y. Huang, J. Zhang, J. Liu, Z. Li, S. Jin, Z. Li, S. Zhang, H. Zhou, *Mater Today Energy*. 2019, **14**, 100349.
14. W. Xu, C. Liu, Q. Wu, W. Xie, W-Y. Kim, S-Y Lee, J. Gwone, *J. Mater. Chem. A*, 2020, **8**, 18327.
15. Z. Li, G. Zhou, L. Ye, J. He, W. W Xu, S. Hong, W. Chen, M-C. Li, C. Liu, C. Mei, *Chem Eng J.*, 2023, **472**, 144992.
16. Y. Mao, H. Ren, J. Zhang, T. Luo, N. Liu, B. Wang, S. Le, N. Zhang, *Electrochim Acta*, 2021, **393**, 139094.
17. H. Zhang, X. Gan, Z. Song, J. Zhou, *Angew. Chem.Int. Ed.* 2023, **62**, e20221783.
18. C. Jia, X. Zhang, S. Liang, Y. Fu, W. Liu, J. Chen, X. Liu, L. Zhang, *J Power Sources.*, 2022, **548**, 232072.
19. Q. Liu, Z. Ji, F. Mo, W. Ling, J. Wang, H. Lei, M. Cui, Z. Zhang, Y. Liu, L. Cheng, W. Li, Y. Huang, *ACS Appl. Energy Mater.* 2022, **5**, 12448.
20. H. Dong, J. Li, S. Zhao, Y. Jiao, J. Chen, Y. Tan, D. J. L. Brett, G. He, I. P. Parki, *ACS Appl. Mater. Interfaces.*, 2021, **13**, 745.

21. H. Y. Ge, L. Qin, B. Zhang, L. Jiang, Y. Tang, B. Lu, S. Tian, J. Zhou, *Nanoscale Horiz.*, 2024, **9**, 1514
22. G. Li, Z. Zhao, S. Zhang, L. Sun, M. Li, J. A. Yuwono, J. Mao, J. Hao, J (Pimm) Vongsvivut, L. Xing, C-X. Zhao, Z. Guo, *Nat Commun.* 2023, **14**, 6526.
23. Y. Quan, H. Ma, M. Chen, W. Zhou, Q. Tian, X. Han, J. Chen, *ACS Appl. Mater. Interfaces* 2023, **15**, 44974.
24. M. Wu, Y. Zhang, L. Xu, C. Yang, M. Hong, M. Cui, B. C. Clifford, S. He, S. Jing, Y. Yao, L. Hu, *Matter* 2022, **5**, 3402
25. Y. Quan, W. Zhou, T. Wu, M. Chen, X. Han, Q. Tian, J. Xu, J. Chen, *Chem. Eng. J.* 2022, **446**, 137056.
26. Y. Liu, A. Gao, J. Hao, X. Li, J. Ling, F. Yi, Q. Li, D. Shu, Soaking-free and self-healing hydrogel for wearable zinc-ion batteries, *Chem Eng J.*, 2023, **452**, 139605.
27. Y. Deng, Y. Wu, L. Wang, K. Zhang, Y. Wang, L. Yan, *J Colloid Interface Sci.*, 2023, 633, 142.
28. N. Mittal, A. Ojanguren, D. Kundu, E. Lizundia, M. Niederberger, *Small* 2023, **19**, 2206249.
29. P. Sun, W. Liu, D. Yang, Y. Zhang, W. Xiong, S. Li, J. Chen, J. Tian, L. Zhang, *Electrochim Acta.*, 2022, **429**, 140985.
30. Z. Zheng, W. Shi, X. Zhou, X. Zhang, W. Guo, X. Shi, Y. Xiong, Y. Zhu, *iScience*, 2023, **26**, 106437.
31. A. Lahiri, L. Yang, O. Höfft, F. Endres, *Mater. Adv.*, 2021, **2**, 2676.
32. D. Kumar, L. R. Franco, N. Abdou, R. Shu, A. Martinelli, C. M. Araujo, J. Gladisch, V. Gueskine, R. Crispin, Z. Khan, *Energy Environ. Mater.* 2024, 0, e12752, <https://doi.org/10.1002/eem2.12752>.
33. N. Patil, C. de la Cruz, D. Ciurduc, A. Mavrandonakis, J. Palma, R. Marcilla, *Adv. Energy Mater.* 2021, **11**, 2100939.

34. A. Swiderska-Mocek, P. Jakobczyk, A. Lewandowski, *J Solid State Electrochem*, 2017, **21**, 2825.
35. D. D. S. Argyropoulos, C. Crestini, C. Dahlstrand, E. Furusjö, C. Gioia, K. Jedvert, G. Henriksson, C. Hulteberg, M. Lawoko, C. Pierrou, J. S. M. Samec, E. Subbotina, H. Wallmo, M. Wimby, *ChemSusChem* 2023, **16**, e202300492
36. P.S. Chauhan, R. Agrawal, A. satlewal, R. Kumar, R. P. Gupta, S.S.V. Ramakumar, *Int. J. Biol. Macromol.*, 2022, **197**, 179.
37. V. K. Garlapati, A.K. Chandel, S.P. J. Kumar, S. Sharma, S. Sevda, A. P. Ingle, D. Pant, *Renew. Sust. Energ. Rev.*, 2020, **130**, 109977.
38. M. Muddasar, M. Culebras, M. N. Collins, *Mater. Today Sustain.* 2024, **28**, 100990
39. F. Santos, A. Urbina, J. Abad, R. López, C. Toledo, A.J. Fernández Romero, *Chemosphere* 2020, **250**, 126273.
40. M. Iturronobeitia, O. Akizu-Gardoki, O. Amondarain, R. Minguez, E. Lizundia, *Adv. Sustainable Syst.* 2022, **6**, 2100308.
41. R. Zhang, Q. Wang, H. Shen, Y. Yang, P. Liu, Y. Dong, *Algal. Res.*, 2024, **78**, 103384.