Supplementary Material

Materials and Structure Design for Solid-State Zinc-Ion Batteries: A Mini-Review

Evan Hansen1, Jian Liu1\*

1School of Engineering, Faculty of Applied Science, the University of British Columbia, Kelowna, B.C., Canada

**\* Correspondence:**Jian Liu
Jian.liu@ubc.ca



**Supplementary Figure 1** – Schematics of (a) gel polymer electrolyte (GPE) and (b) solid polymer electrolyte (SPE) structures.

**Supplementary Table-1** Summary of gel polymer electrolytes (GPEs) and solid polymer electrolytes (SPEs) for solid-state Zn-ion batteries (SSZIBs).

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| Type | Polymer | Salt | Plasticizer | Ionic Conductivity (mS cm-1 at RT or 30 °C) | Characteristics | Ref. |
| GPE | PAM | ZnSO4/MnSO­4 | Water | 17.3 | Flexible, stretchable | [1, 2] |
|  | Alginate/PAM | ZnSO4/MnSO4 | Water | 43.2 | Flexible, stretchable, tough, compressible | [3] |
|  | gelatine-g-PAM/PAN | ZnSO4/MnSO4 | Water | 17.6 | Flexible, combined separator/electrolyte | [4] |
|  | PAN-S | ZnSO4 | Water | 3.32 | Combined separator/electrolyte, dendrite suppression | [5] |
|  | PEO/PVdF | Zn(CF3SO3)2 | DMF/EMIMTFSI | 0.163  | Combined separator/electrolyte | [6] |
|  | PEO/PVdF | Zn(CF3SO3)2 | DMF | 0.025 | Combined separator/electrolyte | [7] |
|  | PEO-PPO-PEO | Li2SO4/ZnSO4 | Water | 6.33 | Flexible, dendrite and side-reaction suppression, self-healing electrode/electrolyte interface | [8] |
|  | PEGDGE | Zn(CF3SO3)2 | PC | 0.377 | Flexible, high thermal and electrochemical stability, side-reaction suppression and anti-aging | [9] |
|  | PVdF-HFP/PEO | Zn(BF4)2 | EMIM BF4 | 16.9 | Flexible, tough, combined separator/electrolyte, high thermal stability, dendrite and side-reaction suppression | [10] |
|  | PVA | Zn(CF3SO3)2 | Water | 12.6 | Flexible, self-healing | [11] |
|  | PVA | KCl/Zn(CH3COO)2 | Water | - | Flexible, combined separator/electrolyte, chromatic short-circuit warning | [12] |
|  | PVA | LiCl/ZnCl2/MnSO4 | Water | - | Flexible, dendrite and side-reaction suppression | [13] |
|  | PVA | Zn(CF3SO3)2/MnCl2 | Water | - | Flexible | [14] |
|  | PVA | LiCl/ZnCl2 | Water | - | Flexible | [14] |
|  | PVC/PEMA | Zn(CF3SO3)2 | DMF/EMIMTFSI | 0.110 | Flexible, combined separator/electrolyte | [15, 16] |
|  | PVC/PEMA with SiO2 nanofiller | Zn(CF3SO3)2 | DMF/EMIMTFSI | 0.671 | Flexible | [17] |
|  | PVdF-HFP | Zn(TFSI)2 | EC/PEGDME | 0.47 | - | [18] |
|  | PVdF-HFP | Zn(TFSI)2 | EMITFSI | 1.05 | Flexible, high thermal stability | [19] |
|  | PVdF-HFP | Zn(CF3SO3)2 | EMITF | 1.31 | Flexible, high thermal stability | [19] |
|  | PVdF-HFP with ZnO nanofiller | Zn(CF3SO3)2 | EC/PC | 6.70 | Combined separator/electrolyte | [20] |
|  | PVdF-HFP | ZN(CF3SO3)2 | NMP/EMIMTFSI | 3.82 | - | [21] |
|  | PVdF-HFP | ZN(CF3SO3)2 | NMP/EMIMTF | 7.07 | - | [21] |
|  | PVdF-HFP | ZN(CF3SO3)2 | THF/EMITF | 0.144 | Flexible  | [22] |
|  | FS | ZnSO4/Na2SO4 | Boric Acid/Water | 8.1 | Flexible, dendrite suppression | [23] |
|  | FS | Li2SO4/ZnSO4 | PEG300/Water | - | Dendrite and side-reaction suppression | [24] |
|  | FS with Pyrazole additive | Li2SO4/ZnSO4 | Water | - | Dendrite and side-reaction suppression | [25] |
|  | PNA | ZnSO4/MnSO­4 | DMF/Water | - | Thermal smart protection (solid above 50˚C with low conductivity) | [26] |
|  | Gelatin | ZnSO4/Li2SO4 | Water | 6.15 | Flexible, compressible, tough, brittle, dendrite suppression | [27] |
|  | EG-waPUA/PAM | ZnSO4/MnSO4 | Water | 16.8 | Flexible, stretchable, compressible, tough, combined separator/electrolyte, operational in sub-zero temps. | [28] |
|  | NFC/PAM | ZnSO4/MnSO4 | Water | 22.8 | Flexible, stretchable, tough | [29] |
|  | Xanthan Gum | ZnSO4/MnSO4 | Water | 16.5 | Flexible, combined separator/electrolyte, non-toxic, dendrite and side-reaction suppression | [30] |
|  | KCR | ZnSO4/MnSO4 | Water | 33.2 | Flexible, combined separator/electrolyte, non-toxic | [31] |
| SPE | PEO | ZnCl2 | N/A | ~3.00 x 10-6  | - | [32] |
|  | PEO | ZnBr2 | N/A | ~7.00 x 10-6 | - | [32] |
|  | PEO | ZnI2 | N/A | ~7.00 x 10-6 | - | [32] |
|  | PEOsynthesis by solution casting | Zn(CH3COO)2 | N/A | 1.55 x 10-3 | - | [33] |
|  | PEOsynthesis by hot-press casting | Zn(CH3COO)2 | N/A | 1.15 x 10-4 | - | [34] |
|  | PEO | Zn(CF3SO3)2 | N/A | 1.09 x 10-3 | - | [35] |
|  | PEO/PVdF | Zn(CF3SO3)2 | N/A | 0.025 | - | [7] |
|  | d-U(2000)60PEO | Zn(CF3SO3)2 | N/A | 2.70 x 10-3 | High thermal stability | [36] |
|  | PEO/PPG with Al2O3 nanofiller | Zn(CF3SO3)2 | N/A | 0.210 | High thermal and electrochemical stability | [37] |
|  | Crosslinked PEO with TiO2 nanofiller | ZnCl2 | N/A | ~1 | High thermal stability  | [38] |
|  | PEO with BANFs | Zn(CF3SO3)2 | N/A | 2.5 x 10-2 | Flexible, tough, compressible, dendrite suppression | [39] |
|  | PVdF-HFP | Zn(CF3SO3)2 | N/A | 0.0244 | Flexible, high thermal and electrochemical stability, dendrite suppression | [40] |
|  | PVdF-HFP with ZrO2 nanofiller | ZrO2/Zn(CF3SO3­)2 | N/A | 0.46 | High thermal and electrochemical stability | [41] |
|  | PVdF-HFP with TiO2 nanofiller | Zn(CF3SO3­)2 | N/A | 0.34 | - | [42] |
|  | PVC/PEMA | Zn(CF3SO3­)2 | N/A | 2.79 x 10-3 | - | [15] |
|  | ZnMOF-808 | ZrOCl2·8H2O | N/A | 0.21 | Dendrite suppression | [43, 44] |
|  | CMC | ZnSO4 | N/A | - | Flexible, coaxial arrangement | [45] |
|  | CMC/PniPAM20 | Zn(CF3SO3)2 | N/A | 0.168 | Flexible, tough, high thermal stability, dendrite suppression | [46] |

**References**

1. Li, H.F., et al., Waterproof and Tailorable Elastic Rechargeable Yarn Zinc Ion Batteries by a Cross-Linked Polyacrylamide Electrolyte. Acs Nano, 2018. **12**(4): p. 3140-3148.

2. Wang, Z.F., et al., Highly Compressible Cross-Linked Polyacrylamide Hydrogel-Enabled Compressible Zn-MnO2 Battery and a Flexible Battery-Sensor System. Acs Applied Materials & Interfaces, 2018. **10**(51): p. 44527-44534.

3. Liu, Z.X., et al., A mechanically durable and device-level tough Zn-MnO2 battery with high flexibility. Energy Storage Materials, 2019. **23**: p. 636-645.

4. Li, H.F., et al., An extremely safe and wearable solid-state zinc ion battery based on a hierarchical structured polymer electrolyte. Energy & Environmental Science, 2018. **11**(4): p. 941-951.

5. Lee, B.S., et al., Dendrite Suppression Membranes for Rechargeable Zinc Batteries. Acs Applied Materials & Interfaces, 2018. **10**(45): p. 38928-38935.

6. Rathika, R. and S.A. Suthanthiraraj, Influence of 1-ethyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide plasticization on zinc-ion conducting PEO/PVdF blend gel polymer electrolyte. Journal of Materials Science-Materials in Electronics, 2018. **29**(23): p. 19632-19643.

7. Rathika, R., O. Padmaraj, and S.A. Suthanthiraraj, Electrical conductivity and dielectric relaxation behaviour of PEO/PVdF-based solid polymer blend electrolytes for zinc battery applications. Ionics, 2018. **24**(1): p. 243-255.

8. Zhao, J., et al., A Smart Flexible Zinc Battery with Cooling Recovery Ability. Angewandte Chemie, 2017. **129**(27): p. 7979-7983.

9. Dong, H., et al., An anti-aging polymer electrolyte for flexible rechargeable zinc-ion batteries. Journal of Materials Chemistry A, 2020.

10. Ma, L., et al., Hydrogen-Free and Dendrite-Free All-Solid-State Zn-Ion Batteries. Adv Mater, 2020. **32**(14): p. e1908121.

11. Huang, S., et al., A Self-Healing Integrated All-in-One Zinc-Ion Battery. Angewandte Chemie-International Edition, 2019. **58**(13): p. 4313-4317.

12. Wang, J.Q., et al., A flexible, electrochromic, rechargeable Zn//PPy battery with a short circuit chromatic warning function. Journal of Materials Chemistry A, 2018. **6**(24): p. 11113-11118.

13. Zeng, Y.X., et al., Dendrite-Free Zinc Deposition Induced by Multifunctional CNT Frameworks for Stable Flexible Zn-Ion Batteries. Advanced Materials, 2019. **31**(36).

14. Wang, K., et al., High-Performance Cable-Type Flexible Rechargeable Zn Battery Based on MnO2@CNT Fiber Microelectrode. Acs Applied Materials & Interfaces, 2018. **10**(29): p. 24573-24582.

15. Prasanna, C.M.S. and S.A. Suthanthiraraj, Effective influences of 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide (EMIMTFSI) ionic liquid on the ion transport properties of micro-porous zinc-ion conducting poly (vinyl chloride)/poly (ethyl methacrylate) blend-based polymer electrolytes. Journal of Polymer Research, 2016. **23**(7).

16. Prasanna, C.M.S. and S.A. Suthanthiraraj, Dielectric and thermal features of zinc ion conducting gel polymer electrolytes (GPEs) containing PVC/PEMA blend and EMIMTFSI ionic liquid. Ionics, 2018. **24**(9): p. 2631-2646.

17. Murali, S.P.C. and A.S. Samuel, Zinc ion conducting blended polymer electrolytes based on room temperature ionic liquid and ceramic filler. Journal of Applied Polymer Science, 2019. **136**(24).

18. Ye, H. and J.J. Xu, Zinc ion conducting polymer electrolytes based on oligomeric polyether/PVDF-HFP blends. Journal of Power Sources, 2007. **165**(2): p. 500-508.

19. Xu, J.J., H. Ye, and J. Huang, Novel zinc ion conducting polymer gel electrolytes based on ionic liquids. Electrochemistry Communications, 2005. **7**(12): p. 1309-1317.

20. Sellam and S.A. Hashmi, Enhanced zinc ion transport in gel polymer electrolyte: effect of nano-sized ZnO dispersion. Journal of Solid State Electrochemistry, 2012. **16**(9): p. 3105-3114.

21. Tafur, J.P., F. Santos, and A.J.F. Romero, Influence of the Ionic Liquid Type on the Gel Polymer Electrolytes Properties. Membranes, 2015. **5**(4): p. 752-771.

22. Liu, J., et al., Ionic Liquid-Incorporated Zn-Ion Conducting Polymer Electrolyte Membranes. Polymers (Basel), 2020. **12**(8).

23. Chao, D.L., et al., A High-Rate and Stable Quasi-Solid-State Zinc-Ion Battery with Novel 2D Layered Zinc Orthovanadate Array. Advanced Materials, 2018. **30**(32): p. 7.

24. Mitha, A., et al., Thixotropic gel electrolyte containing poly(ethylene glycol) with high zinc ion concentration for the secondary aqueous Zn/LiMn2O4 battery. Journal of Electroanalytical Chemistry, 2019. **836**: p. 1-6.

25. Hoang, T.K.A., et al., Sustainable Gel Electrolyte Containing Pyrazole as Corrosion Inhibitor and Dendrite Suppressor for Aqueous Zn/LiMn2O4 Battery. Chemsuschem, 2017. **10**(13): p. 2816-2822.

26. Mo, F.N.A., et al., A smart safe rechargeable zinc ion battery based on sol-gel transition electrolytes. Science Bulletin, 2018. **63**(16): p. 1077-1086.

27. Han, Q., et al., Durable, flexible self- standing hydrogel electrolytes enabling high- safety rechargeable solid- state zinc metal batteries. Journal of Materials Chemistry A, 2018. **6**(45): p. 23046-23054.

28. Mo, F.N., et al., A flexible rechargeable aqueous zinc manganese-dioxide battery working at-20 degrees C. Energy & Environmental Science, 2019. **12**(2): p. 706-715.

29. Wang, D.H., et al., A Nanofibrillated Cellulose/Polyacrylamide Electrolyte-Based Flexible and Sewable High-Performance Zn-MnO2 Battery with Superior Shear Resistance. Small, 2018. **14**(51).

30. Zhang, S.L., et al., An adaptive and stable bio-electrolyte for rechargeable Zn-ion batteries. Journal of Materials Chemistry A, 2018. **6**(26): p. 12237-12243.

31. Huang, Y., et al., Flexible quasi-solid-state zinc ion batteries enabled by highly conductive carrageenan bio-polymer electrolyte. Rsc Advances, 2019. **9**(29): p. 16313-16319.

32. Yang, H. and G.C. Farrington, POLY(ETHYLENE OXIDE)-BASED ZN(II) HALIDE ELECTROLYTES. Journal of the Electrochemical Society, 1992. **139**(6): p. 1646-1654.

33. Polu, A.R., R. Kumar, and G.M. Joshi, Effect of zinc salt on transport, structural, and thermal properties of PEG-based polymer electrolytes for battery application. Ionics, 2014. **20**(5): p. 675-679.

34. Karan, S., et al., Investigations on Ion Transport Behaviour in a Non-Lithium Chemical Based Solid Polymer Electrolyte (SPE): PEO:ZnA. Materials Today-Proceedings, 2016. **3**(2): p. 109-114.

35. Karan, S., et al., Characterization of ion transport property in hot-press cast solid polymer electrolyte (SPE) films: PEO: Zn(CF3SO3)(2). Ionics, 2017. **23**(10): p. 2721-2726.

36. Nunes, S.C., et al., Study of sol-gel derived di-ureasils doped with zinc triflate. Solid State Sciences, 2006. **8**(12): p. 1484-1491.

37. Nancy, A.C. and S.A. Suthanthiraraj, Effect of Al2O3 nanofiller on the electrical, thermal and structural properties of PEO:PPG based nanocomposite polymer electrolyte. Ionics, 2017. **23**(6): p. 1439-1449.

38. Pucic, I. and A. Turkovic, Radiation modification of (PEO)(8)ZnCl2 polyelectrolyte and nanocomposite. Solid State Ionics, 2005. **176**(19-22): p. 1797-1800.

39. Wang, M.Q., et al., Biomimetic Solid-State Zn2+ Electrolyte for Corrugated Structural Batteries. Acs Nano, 2019. **13**(2): p. 1107-1115.

40. Liu, J., et al., Fabrication and characterization of Zn-ion-conducting solid polymer electrolyte films based on PVdF-HFP/Zn(Tf)2 complex system. Journal of Materials Science: Materials in Electronics, 2020. **31**(8): p. 6160-6173.

41. Johnsi, M. and S.A. Suthanthiraraj, Compositional effect of ZrO2 nanofillers on a PVDF-co-HFP based polymer electrolyte system for solid state zinc batteries. Chinese Journal of Polymer Science, 2016. **34**(3): p. 332-343.

42. Johnsi, M. and S.A. Suthanthiraraj, Preparation, zinc ion transport properties, and battery application based on poly(vinilydene fluoride-co-hexa fluoro propylene) polymer electrolyte system containing titanium dioxide nanofiller. High Performance Polymers, 2015. **27**(7): p. 877-885.

43. Wang, Z.Q., et al., A MOF-based single-ion Zn2+ solid electrolyte leading to dendrite-free rechargeable Zn batteries. Nano Energy, 2019. **56**: p. 92-99.

44. Furukawa, H., et al., Water Adsorption in Porous Metal–Organic Frameworks and Related Materials. Journal of the American Chemical Society, 2014. **136**(11): p. 4369-4381.

45. Zhang, Q.C., et al., Flexible and High-Voltage Coaxial-Fiber Aqueous Rechargeable Zinc-Ion Battery. Nano Letters, 2019. **19**(6): p. 4035-4042.

46. Dueramae, I., et al., Properties enhancement of carboxymethyl cellulose with thermo-responsive polymer as solid polymer electrolyte for zinc ion battery. Scientific Reports, 2020. **10**(1).