

High performance Zn-based batteries using 3D monolithic sponge anodes

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Zinc-based batteries (e.g., Zn–air, Ag–Zn, Ni–Zn) have the ability to overcome some of the major limitations plaguing Li-ion batteries: safety concerns associated with toxic and flammable electrolytes, high material and manufacturing costs, and specific energy generally $< 200 \text{ Wh kg}^{-1}$. In contrast, Zn–air cells, provide significantly higher specific energy (400 Wh kg^{-1}), with the advantages of using safe, low-cost components and an aqueous electrolyte. Broader application of Zn-based batteries is hindered by the limited rechargeability and modest utilization (typically $< 60\%$ of theoretical discharge capacity).^{2,3}

The non-ideal performance of Zn in alkaline electrolytes is attributed to the ad hoc manner in which composite powdered-bed Zn electrodes (with binders and gelling agents) are commonly fabricated. During repeated cycling of these types of anode composites, morphological changes become pronounced, particularly at points of high current density, eventually electrogenerating dendrites that pierce the separator and cause the battery to short.⁴ We apply a 3D architectural redesign of the zinc anodes, focusing on a Zn “sponge” form factor comprising a monolith of interpenetrating, co-continuous networks of solid and void. The benefits of 3D architectures in the development of high-performance anode materials have been noted previously.^{5,6,7,8,9} The continuous conductive Zn networks of the sponge structure facilitates homogeneous current distribution throughout the volume of the electrode structure,¹⁰ a design factor that will minimize uneven reaction loci, which otherwise spurs formation of dendrites during cycling composite powdered-bed Zn electrodes. The confined volume of the void space within the Zn sponge promotes a more controlled electrodeposition of ZnO upon discharge, thereby minimizing shape change. These zinc sponge electrodes will enhance specific power, specific energy, and rechargeability in next-generation zinc-containing batteries.

Our optimized fabrication methods yield zinc sponges electrodes that have minimal ZnO content

and interconnected voids sized at 10–75 μm , providing a highly conductive scaffolding wired in 3D that increases Zn utilization to $\sim 90\%$, and suppresses dendrite formation even after dozens of cycles. We use electron microscopy and X-ray diffraction to assess the structural properties of the zinc sponge at various steps of fabrication and after electrochemical cycling. Electrochemical evaluation is performed in flooded half-cell configurations and in full-cell Zn–air and Ag–Zn prototypes.

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References

1. J.-S. Lee, S. T. Kim, R. Cao, N.-S. Choi, M. Liu, K. T. Lee, and J. Cho. *Adv. Energy Mater.* **18**, 1 (2006).
2. X. Zhang. *J. Power Sources.* **163**, 591 (2006).
3. K. Harting, U. Kunz, T. Turek, *Z. Phys. Chem.* **226**, 151 (2012).
4. J. E. Oxley, C. W. Fleishmann, *Improvement of zinc electrodes for electrochemical cells*. First, Second, and Third Quarterly Reports, N66-13568, N66-16956, and N66-26870 (1965–1966).
5. J.-F. Drillet, M. Adam, S. Barg, A. Herter, D. Koch, V. M. Schmidt, M. Wilhelm. *ECS Trans.* **28**, 13 (2010).
6. J. W. Long, B. Dunn, D. R. Rolison, H. S. White, *Chem. Rev.* **104**, 4463–4492 (2004).
7. F. Chamran, Y. Yeh, H.-S. Min, B. Dunn, C.-J. Kim, *J. Microelectromech. Syst.* **16**, 844 (2007).
8. B. Dunn, C.-J. Kim, S. Tolbert, *IEEE, MEMS2010*, 164–16.
9. F. Chamran, H.-S. Min, B. Dunn, C.-J. Kim, *IEEE, MEMS2007*, 871–874.
10. Z. Nagy, J.O'M. Bockris, *J. Electrochem. Soc.* **119**, 1129 (1972).