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Advances in Alkaline Storage Batteries and their Potential Impact for Society

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For energy storage to become ubiquitous in the electric grid, safe, reliable low cost electrochemical storage technologies that can be manufactured at high volumes with low capital expenditures are needed. Rechargeable alkaline batteries based on abundant and low cost materials with high capacities, such as a Zn anode (820 mAh g^{-1}) paired with a MnO_2 (616 mAh g^{-1}) or S cathode (1675 mAh g^{-1}, based on the idealized redox couple of S^{2-}/S) could serve as high energy dense systems if sufficient cycle life and energy densities can in fact be realized. Alkaline-based cells are also inherently safe and do not have the temperature limitations of Li-ion or Pb-acid batteries, thereby removing the need for complicated thermal management systems, and providing for simpler systems with lower integration costs. Historically Zn/MnO_2 and Zn/S have been primary cells. In this presentation we will cover ongoing efforts to improve the cycle life and active materials utilization (i.e. energy density) in rechargeable Zn/MnO_2 and then report on the first use of a solid-state sulphide/polysulphide electrochemical couple(s) in new rechargeable alkaline Zn/Cu_2S batteries.

Secondary Zn/MnO_2 batteries have in fact been realized when only a small fraction of the theoretical capacity of MnO_2 (≤ 20%) and Zn (≤ 2.5% of Zn capacity) is accessed during each cycle, resulting in ~1000–3000 cycles. These so called limited depth-of-discharge (DOD) Zn/MnO_2 batteries, which aim to retain the γ-MnO_2 phase through the proton insertion and de-insertion cycling process, are now being commercialized, with cycled energy densities of ~ 10-40 Wh L^{-1} at overall estimated costs of ~ \$150-250 kWh^{-1}.[1] Higher energy dense Zn/MnO_2 batteries, that take advantage of the equivalent of full 2-electron cycling between Bi- and Cu-stabilized MnO_2 an $Mn(OH)_2$ are also currently under development[2] with the goal of reaching \$50/kWh at the cell level.[1] However, the fundamental limitations of this battery chemistry needs further work in order to reliably realize > 5000 cycles, which equates to ~ 10-15 years of battery life. Current investigations include utilizing DFT calculations to better understand the cathode cycling process,[3] examining additives to increase the efficiency and cycle life of limited DOD Zn/MnO_2[4] and developing new separators that

prevent the diffusion of soluble deleterious zinc to the cathode.[5] Various aspects of this work will be presented.

In addition to MnO_2, sulphur (S) also has a suitable terrestrial abundance and overall economics for wide-spread battery use; however, to date Zn/S batteries have been hindered by sulphide crossover, which reacts with the Zn anode during discharge, forming an insulating ZnS layer rendering the Zn anode inert to re-charge. In this talk we will also report on our first use of a solid-state sulphide/polysulphide electrochemical couple(s) in alkaline electrolyte.[6] Specifically, a new battery chemistry that consists of a solid-state Cu_2S cathode paired with a Zn anode in alkaline electrolyte will be presented. Zn/Cu_2S batteries cycled between 1.45 V and 0.4 V vs Zn displayed capacities of ~ 1500 mAh g^{-1} (based on mass of S) or ~300 mAh g^{-1} (based on mass of Cu_2S) and high areal (> 23 mAh cm^{-2}) and energy densities (> 135 Wh L^{-1}), but suffered from short cycle life. Efforts to increase the cycle life have demonstrated Zn/Cu_2S batteries with areal capacities of 8.3 mA h cm^{-2} and grid relevant energy density of > 42 Wh L^{-1} after 450 cycles. These results represent the first example of a rechargeable solid-state sulphur cathode in an alkaline battery and augur for future work into increasing the cycle life of the cell chemistry. Various aspects of the battery cycling properties will be reported.

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References

[1] S. Banerjee, *Alkaline Zn-MnO_2 Battery Development: A University-Private-Public Partnership*, in Department of Energy Office of Electricity and Energy Reliability Peer Review, Santa Fe, NM, September 25-27th, 2018., https://eesat.sandia.gov/wp-content/uploads/2018/10/1_SanjoyBanerjee_Presentation.pdf

[2] G. G. Yadav, J. W. Gallaway, D. E. Turney, M. Nyce, J. C. Huang, X. Wei, S. Banerjee, Nat. Commun: 8 (2017).

[3] I. Vasiliev, B. A. Magar, J. Duay, T. N. Lambert, B. Chalamalu, J. Electrochem. Soc: 165 (14,) A3517-A3524 (2018).

[4] M. Kelly, J. Duay, T. N. Lambert, R. Aidun, J. Electrochem. Soc: 164 (14) A3684-A3691, (2017).

[5] J. Duay, M. Kelly and T. N. Lambert, J. Power Sources, *395*, 430–438 (2018).

[6] J. Duay, T. N. Lambert, M. A. Kelly, I. Pineda-Dominguez, J. Electrochem. Soc: manuscript in press (2019).

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