Material Engineering of Anodes for Aqueous Batteries with Enhanced Performance for Aerospace Applications

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Source: Federal Aviation Administration, Security and Hazardous Materials Safety

Last updated November 15, 2024

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Revisiting pre-Li technologies that are intrinsically safer (all aqueous)

- Nickel metal hydride (NiMH) batteries have been used in space applications, including the Horyu-4 satellite and the NOZOMI mission: NOZOMI: The first mission to use NiMH cells in space, launched in 1998 Horyu-4: Used NiMH batteries in its design
- Silver-zinc batteries are often used in space applications because they are lightweight, compact (1/3 the size of NiCd batteries), and powerful: The first battery used in space was a silver-zinc battery in the Russian spacecraft Sputnik in 1957.
- Enhance their rechargeability and utilization
- Mars surface T varies from -153°C to 20°C Moon surface T varies from -246°C to 127°C

Part I

Enhancing the rechargeability of

high-power nickel metal hydride anode

Part II

Enhancing the rechargeability and utilization of zinc anode

AB₅-type hydrogen storage alloy: La_{9.2}Ce_{6.0}Pr_{0.2}Nd_{0.7}Zr_{0.3}Ni_{73.0}Mn_{5.9}Al_{4.6} (excellent low-T rate capability)





Z. Chen, H. Liu, J. Nei, N. Liu*, *Nano Research* 2024, 17, 8819–8825





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Part I

Enhancing the rechargeability of

high-power nickel metal hydride anode

Part II

Enhancing the rechargeability and utilization of zinc anode

Intrinsic flammability of Li-ion & opportunity of Zn-based aqueous batteries







Irreversibility of Zn anode in alkaline electrolyte Root cause #1: ZnO passivation



- Cannot deeply discharge (low utilization)
- Cannot recharge (poor reversibility)

Z.-H. Wu, Y. Zhang, N. Liu*, *Mater. Today Nano* 6, 100032 (2019)

Introducing conductive host to recharge ZnO



Z. Zhou, Y. Zhang, N. Liu*, et al. *Chem. Eng. Sci.* 194, 142-147 (2019)

Only utilize the surface \rightarrow fully utilize the bulk

(Breaking the tradeoff between utilization and rechargeability)



ZnO critical passivation thickness:

~2um

Our hypothesis:

Decreasing the feature size of Zn/ZnO to under 2um can avoid passivation

Irreversibility of Zn anode in alkaline electrolyteRoot cause #1:Root cause #2:ZnO passivationZincate dissolution

200 nm



Carbon paper

Zn(OH)42-

 $ZnO + H_2O + 2OH^- \leftrightarrow Zn(OH)_4^{2-}$

 $Zn(OH)_4^{2-} + 2e^- \leftrightarrow Zn + 4OH^-$

Sealed ZnO nanorod anode



Sealed ZnO nanorod anode





Most previous articles

rsh testing condition: linimum electrolyte o ZnO saturation D0% depth-of-discharge



Irreversibility of Zn anode in alkaline electrolyteRoot cause #1:Root cause #2:Root cause #3:ZnO passivationZincate dissolutionHydrogen evolution



Y. Zhang, A. Mathur, N. Liu* et al. *J. Power Sources* 491, 229547 (2021)

HER-suppressing sealed nanosized (HSSN) zinc anode



Y. Zhang, N. Liu* et al. *Nano Lett.* 20 (6), 4700–4707 (2020)

HER-suppressing sealed nanosized (HSSN) zinc anode



Y. Zhang, N. Liu* et al. *Nano Lett.* 20 (6), 4700–4707 (2020)

Particle-based anode material: ZnO @ ion-sieving carbon



Y. Wu, N. Liu*, et al. *Adv. Energy Mater.* 8 (36), 1802470 (2018)

Further suppression of $Zn(OH)_4^{2-}$ dissolution: Pomegranate-structured ZnO/C anode (Zn-Pome)



P. Chen, Y. Wu, N. Liu*, et al. J. Mater. Chem. A 6 (44), 21933-21940 (2018)

Soluble zincate: Passive encapsulation → Active management



Alloy-seeded Zn anode: mechanism



Y. Zhang, N. Liu* et al. *ACS Energy Lett.* 2021, 6 (2), 404–412

Covalent organic framework (COF) coating

Another approach to control morphology of Zn electrodeposits III. Cyclability I. Zn deposition II. Nucleation & Growth Poor & Short Inhomogeneous Without COF Short-circuit -* Zn2+ Zn2+ Zn2+ Pits Zn2+ Zn2+ Dead Zn 100 nm thick deposits COF film dip-coated onto Zn Homogeneous Stable With COF Zn2+ Zn2+ Zn24 Compact Zn Screened nine COFs Zn2+ Zn2+ Zn2+ Zn2+ Zn2+ Zn2+ Smooth surface deposits with 1-10 nm pore aperture. The best performing one has: 1. Hydrophobic pores 2. Affinity to Zn²⁺ Cathode Anode Separator COF film

Park, Kwak, Hwang, Kang, Liu, Jang, Grzybowski, Adv. Mater. 33 (34), 2101726 (2021)

Covalent organic framework (COF) coated Zn foil anode



Park, Kwak, Hwang, Kang, Liu, Jang, Grzybowski, *Adv. Mater.* 33 (34), 2101726 (2021)

Inhibiting Jahn–Teller distortion in Mn-based cathode



Nam, Hwang, Jang, Kane, Ahn, Kwak, Luo, Li, Kim*, N. Liu*, M. Liu*, *Small* 2024, 20, 2306919

Summary: material engineering enables deeply rechargeable NiMH and Zn anodes in alkaline electrolyte



Acknowledgement

Yamin ZhangYutong WuZhitao ChenEvan WilsonTzu-Ho WuHuitian LiuYuju JeonPeng ChenZhubo ZhouYu YanCollaborators:Prof. Joshua Howe (Texas Tech University)Dr. Timothy Lambert (Sandia National Labs)

Sponsors of this research:



