

Zincate-Blocking-Functionalized Polysulfone Separators for Secondary Zn–MnO₂ Batteries

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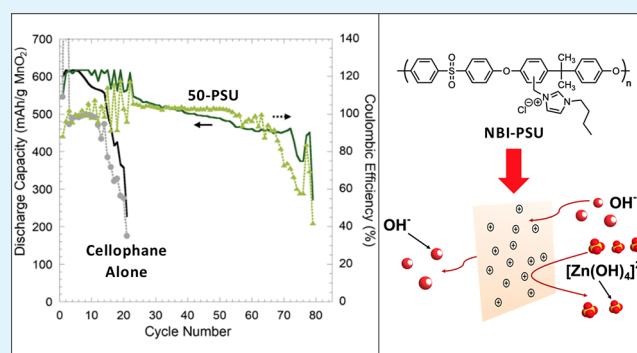
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Supporting Information

ABSTRACT: Alkaline zinc–manganese dioxide (Zn–MnO₂) batteries are well suited for grid storage applications because of their inherently safe, aqueous electrolyte and established materials supply chain, resulting in low production costs. With recent advances in the development of Cu/Bi-stabilized birnessite cathodes capable of the full 2-electron capacity equivalent of MnO₂ (617 mA h/g), there is a need for selective separators that prevent zincate (Zn(OH)₄)²⁻ transport from the anode to the cathode during cycling, as this electrode system fails in the presence of dissolved zinc. Herein, we present the synthesis of *N*-butylimidazolium-functionalized polysulfone (NBI-PSU)-based separators and evaluate their ability to selectively transport hydroxide over zincate. We then examine their impact on the cycling of high depth of discharge Zn/(Cu/Bi–MnO₂) batteries when inserted in between the cathode and anode. Initially, we establish our membranes' selectivity by performing zincate and hydroxide diffusion tests, showing a marked improvement in zincate-blocking (D_{Zn} (cm²/min): $0.17 \pm 0.04 \times 10^{-6}$ for 50-PSU, our most selective separator vs $2.0 \pm 0.8 \times 10^{-6}$ for Cellophane 350P00 and $5.7 \pm 0.8 \times 10^{-6}$ for Celgard 3501), while maintaining similar crossover rates for hydroxide (D_{OH} (cm²/min): $9.4 \pm 0.1 \times 10^{-6}$ for 50-PSU vs $17 \pm 0.5 \times 10^{-6}$ for Cellophane 350P00 and $6.7 \pm 0.6 \times 10^{-6}$ for Celgard 3501). We then implement our membranes into cells and observe an improvement in cycle life over control cells containing only the commercial separators (cell lifetime extended from 21 to 79 cycles).

KEYWORDS: zinc batteries, selective separators, functionalized polysulfone, zincate blocking, crossover, cycle life



INTRODUCTION

As society transitions away from fossil fuels, clean and renewable power sources such as wind and solar energy are increasingly being integrated into electrical grids. However, the intermittent nature of such sources highlights the need for energy storage systems that can collect and/or release electricity when renewable output mismatches transmission capacity or demand. Rechargeable battery-based systems for grid storage are gaining popularity because of their ease of manufacture, scalability to desired capacities, and modularity.

To be successful, a grid-integrated battery system should have a high energy density, a long cycle life (>5000 cycles), a low production cost (<\$100 kW h⁻¹), and minimal hazards.¹ Alkaline zinc–manganese dioxide (Zn–MnO₂) batteries, which have a Zn anode, MnO₂ cathode, and aqueous KOH electrolyte, are a promising candidate if sufficient rechargeability can be achieved.² First patented in 1960 and now ubiquitous as disposable batteries in everyday electronics, primary Zn–MnO₂ batteries have energy densities of up to 400 W h L⁻¹ or 150 W h kg⁻¹, rivaling lithium-ion batteries, along with abundant raw materials and a long-established

supply chain that puts their cost as low as \$20 kW h⁻¹.^{3–5} Furthermore, Zn–MnO₂ batteries have a lower environmental impact than other types of batteries, having a nonflammable aqueous electrolyte and even EPA certification for landfill disposal in the United States.⁶

The biggest challenge in implementing alkaline Zn–MnO₂ batteries in the grid is their historically poor rechargeability because of irreversible processes in each electrode during discharge. In theory, both electrode materials can undergo two-electron redox processes to impart high specific capacities of 820 mA h g⁻¹ for Zn and 617 mA h g⁻¹ for MnO₂. For MnO₂, the first- and second-electron reduction reactions occur by distinct mechanisms, the former through proton intercalation and the latter through dissolution-precipitation. However,

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