Next-Generation Rechargeable Silver–Zinc Batteries Enabled by Interfacial Control and Electrode Redesign

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Abstract: Zinc sponge electrodes pioneered at the US Naval Research Laboratory enable a new family of alkaline zinc-based batteries that will serve as energy/power-capable, but safe alternatives to lithium-ion batteries for critical DoD applications. Recent advances in Zn sponge fabrication yield monolithic form factors using a low cost, scalable, and rapidly manufacturable protocol. When incorporated as the anode in lab-scale silver–zinc cells, Zn sponge electrodes facilitate deep-discharge utilization and high-power operation.

Keywords: silver–zinc batteries, aqueous batteries, architected electrodes, zinc batteries, high-power devices

Introduction

Silver–zinc (Ag–Zn) batteries haves served as a mainstay power source for DoD platforms over the past several decades, providing mission-enabling high-power capability in an energy-dense package.[1] Unlike their lithium-ion counterparts, Ag–Zn batteries employ nonstrategic materials and nonflammable aqueous electrolytes. Despite these performance attributes, the broader application of Ag–Zn batteries is hindered by issues of poor-to-moderate cycle life and shelf life. Contraindicating issues arise from multiple deleterious processes at the Ag/Ag_xO cathode, multilayer separator system, and the Zn anode. Recent breakthroughs at the NRL on a 3D Zn "sponge" (Zn_{NRL}) have largely solved the decades-old problem of shape change at the anode, extending cycle life in rechargeable alkaline Ni–Zn cells[2–4] and promoting high-power discharge in Ag–Zn cells.[5,6] The structure of the sponge with three-dimensional, conductive Zn metal pathways and ample open volume for electrolyte access drastically improves power capability over traditional powder-bed composite or foil anodes. We now report protocols that improve scalability and manufacturability with lower input costs.

Previous-generation Zn_{NRL} fabrication protocols require emulsion-based compositions based on organic pore-forming agents (carboxymethyl cellulose (CMC) or cornstarch). After drying and consolidating the particulate zinc–porogen object, followed by thermal processing under inert gas flow (nitrogen or argon), the organic porogen must then be thermally decomposed in an oxidizing atmosphere. As a consequence, metallic Zn in the sponge may be excessively converted to zinc oxide (ZnO). The entire process is conducted in a sealed tube furnace and takes ~10 h for tube purging, thermal ramping, and cooling.

We now employ a fabrication method that uses a thermally stable, inorganic pore-former to create the interconnected Zn architecture.[7] Incorporation of a thermally stable, chemically removable inorganic porogen significantly reduces the time and temperature of thermal processing and allows the use of a simple box furnace and air atmosphere. The resulting monolithic Zn_{NRL} sponge has controllable ZnO content that influences mechanical strength, allowing a greater range of form factors (shape and size). To benchmark electrochemical performance relative to the previous four generations of Zn_{NRL} sponges, we evaluate "Gen 5" sponges in small-scale primary Ag–Zn cells for such metrics as discharge capacity and rate capability.

Results and Discussion

Zinc sponge electrodes are fabricated by mixing Zn powder and calcium carbonate into a 1 wt% aqueous dispersion of high viscosity CMC. The resulting Zn paste is pressed into an acrylic mold and dried overnight at 50–70°C. The ultimate form factor of the monolith is dictated by the shape and dimensions of the mold. Figure 1 shows example Zn monolith shapes, including cylinders and plates at a variety of size scales.
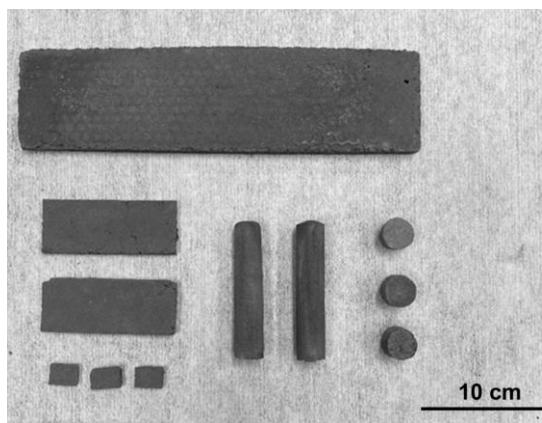

Figure 1. Photograph of Zn_NRL sponge monoliths in various sizes and form factors.

To promote Zn particle fusion, the dried monolithic pre-forms are heated at 580°C for 1 h in air. Thermal processing above the melting point of Zn metal (419°C) greatly improves interparticle connectivity (Figure 2), subsequently enhancing mechanical strength and electronic conductivity. After cooling to room temperature, the $CaCO_3$ porogen is removed by submerging the heat-treated, Zn monoliths in 1 M HCl for 5–10 min followed by thorough rinsing with water and then ethanol; the alcohol promotes drying and limits further oxidation of the Zn surfaces. After thermal treatment and acid washing, the Zn architectures comprise ~80% metallic Zn and ~20% ZnO by weight, according to RIR (reference intensity ratio) fitting of the X-ray diffraction pattern (Figure 3). Previous-generation Zn_NRL fabrication protocols produce monoliths with 25–40% ZnO,[2–6] which may be undesirable for direct incorporation into some alkaline battery configuration.
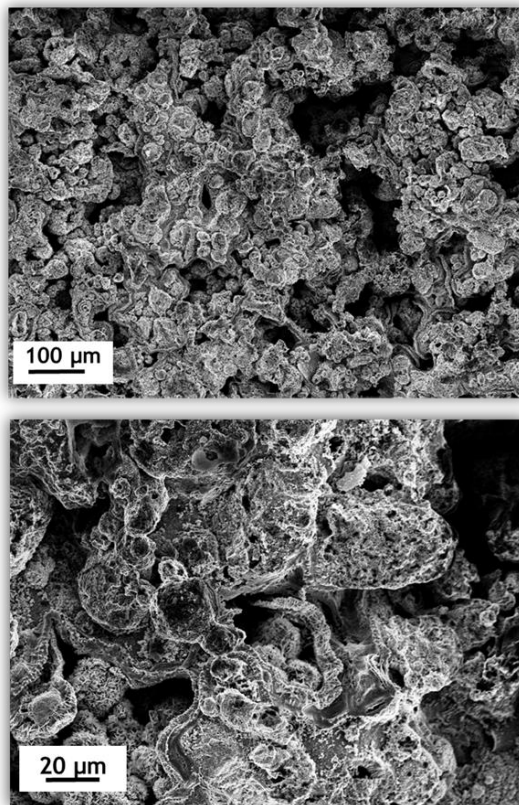

Figure 2. Scanning electron micrographs of Zn_NRL sponge monoliths.

A defining capability of Gen-5 fabrication is the use of $CaCO_3$ as an inorganic porogen. The carbonate provides thermal stability and high aqueous acid solubility—the former permits taking Zn above its melting point while the unaffected $CaCO_3$ retains the form factor, and the latter allows facile removal after thermal processing. The organic porogens used to fabricate Zn-sponge generations 1–4 must be removed with high-temperature oxidative treatment. After removal, only air remains to diffuse heat into the Zn structure, which risks inhomogeneous internal heating and increases the degree of thermal oxidation. Because the thermal conductivity of $CaCO_3$ (2.25 W mK^{-1}) is ~100× greater than that of air (0.025 W mK^{-1}), retaining $CaCO_3$ throughout thermal processing disperses heat more quickly and uniformly within the Zn object to enhance fusion of individual Zn particles into a mechanically cohesive network. The resulting Zn sponge has mechanical strength equal to or greater than those derived from organic porogen–based methods.
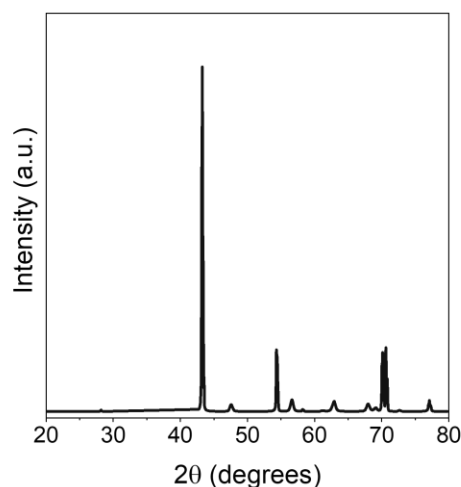
Figure 3. X-ray diffraction (XRD) pattern of Zn_{NRL} monolith after thermal treatment (580°C, 1 h) and removal of $CaCO_3$ porogen (10 min washing in 1 M HCl).

Figure 4. Primary discharge of Zn_{NRL} sponge electrode in a Zn–air cell.

We validate Gen-5 sponges using primary discharge of a Zn–air cell at a modest current density. Unlike Gen-1 and -2 sponges, Gen-5 sponges are not electrochemically pre-reduced before assembling the Zn–air cell. The relatively low ZnO content of Gen-5 enables good physical contact with the current collector of the Zn–air cell, resulting in low ohmic resistance. Primary discharge of these Zn–air cells at 10 mA cm^{-2} shows an expected sloping plateau ~1.2 V, culminating in a specific capacity of 500–550 mAh g$_{Zn}^{-1}$ (Figure 4). Even though the Gen-5 sponges are ~20% ZnO when incorporated into the Zn–air cell, measured capacity is 60–68% of theoretical Zn capacity (819 mAh g^{-1}).

Silver–zinc coin cells are constructed using Gen-5 sponges as the anode and a pellet of silver oxide (Ag_xO) powder pressed at 5 metric tons into Ag mesh as the cathode. Silver and tin foils serve as the positive and negative current collectors, respectively. Even without optimizing the silver oxide cathode, Ag–Zn_{NRL} cells deliver high energy density under extreme current demand (Figure 5). At 0.5 A cm^{-2}, the cell voltage remains above 1 V, resulting in an areal power density >0.5 W cm^{-2}, orders of magnitude more power than Ag–Zn batteries in recent literature.[8,9]
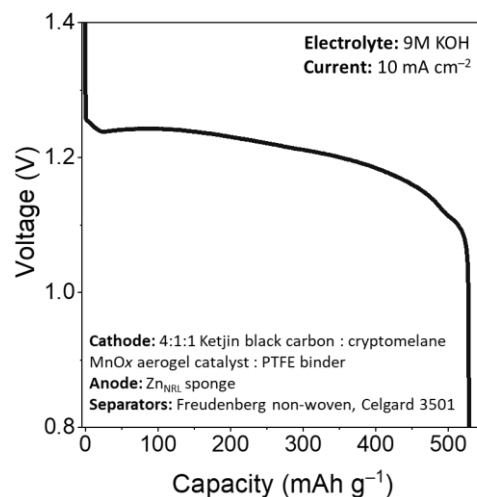

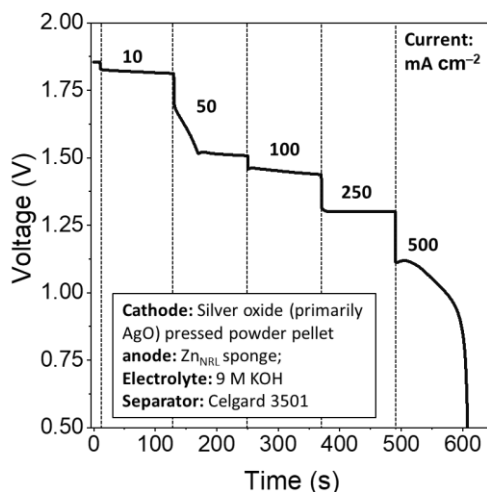**Figure 5.** Galvanostatic staircase discharge of Gen-5 Zn_{NRL} sponge configured in a primary Ag–Zn cell. Geometric area of the anode and cathode were identical (1 cm^2). The Zn_{NRL} sponge is 1 mm thick and the cathode:anode capacity ratio is 1.1:1.

Conclusion

Generation-5 Zn sponge electrodes are rapidly fabricated using cheap, scalable components. Thermal processing in air and subsequent treatment in hydrochloric acid produces porous Zn monoliths that discharge >500 mAh g^{-1}, even with ~20% ZnO to improve mechanical integrity.

Silver–zinc batteries utilizing Zn-sponge anodes and pressed-powder Ag_xO cathodes support current densities >100 mA cm^{-2} and >500 mW cm^{-2}. We posit that redesigning the Ag/Ag_xO cathode in a similar sponge-like construct will further elevate the performance of next-generation Ag–Zn batteries in terms of power output and cyclability in rechargeable configurations.

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