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## Zinc-sponge battery electrodes that suppress dendrites

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**TITLE**

# Zinc-Sponge Battery Electrodes that Suppress Dendrites

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**KEYWORDS**

Rechargeable batteries, zinc sponge, dendrites, shape change, alkaline electrolytes, metal foam, open-cell foam, zinc batteries, nickel–zinc, silver–zinc, zinc–air, sustainable batteries

**SUMMARY**

The goal of the reported protocols is to create rechargeable zinc-sponge electrodes that suppress dendrites and shape change in zinc batteries, such as nickel–zinc or zinc–air.

**ABSTRACT**

We report two methods to create zinc-sponge electrodes that suppress dendrite formation and shape change for rechargeable zinc batteries. Both methods are characterized by creating a paste made of zinc particles, organic porogen, and viscosity-enhancing agent that is heated under an inert gas and then air. During heating under the inert gas, the zinc particles anneal together, and the porogen decomposes; under air, the zinc fuses and residual organic burns out, yielding an open-cell metal foam or sponge. We tune the mechanical and electrochemical properties of the zinc sponges by varying zinc-to-porogen mass ratio, heating time under inert gas and air, and size and shape of the zinc and porogen particles. An advantage of the reported methods is their ability to finely tune zinc-sponge architecture. The selected size and shape of the zinc and porogen particles influence the morphology of the pore structure. A limitation is that resulting sponges have disordered pore structures that result in low mechanical strength at low volume fractions of zinc (<30%). Applications for these zinc-sponge electrodes include batteries for grid-storage, personal electronics, electric vehicles, and electric aviation. Users can expect zinc-sponge electrodes to cycle up to 40% depth of discharge at technologically relevant rates and areal capacities without the formation of separator-piercing dendrites.

## INTRODUCTION

The purpose of the reported fabrication methods is to create zinc (Zn) sponge electrodes that suppress dendrite formation and shape change. Historically, these problems have limited the cycle life of Zn batteries. Zinc-sponge electrodes have resolved these issues, enabling Zn batteries with longer cycle lives[1–6]. The sponge structure suppresses dendrite formation and shape change because (1) the fused Zn framework electrically wires the entire volume of the sponge; (2) the pores hold zincate near the Zn-sponge surface; and (3) the sponge has a high surface area that decreases local current density below values identified to sprout dendrites in alkaline electrolytes[7]. However, if sponge surface area is too high, substantial corrosion occurs[5]. If the sponge pores are too large, the sponge will have a low volumetric capacity[5]. Also, if the sponge pores are too small, the Zn electrode will have insufficient electrolyte to access Zn during discharge, resulting in low power and capacity[5,6].

The rationale behind the reported fabrication methods is to create Zn sponges with appropriate sponge porosities and pore diameters. Experimentally, we find that Zn sponges with porosities from 50 to 70% with pore diameters near 10 μm cycle well in full-cell batteries and display low corrosion rates[5]. We note that existing methods to manufacture commercial metal foams fail to achieve similar morphologies on these length scales[8], so the reported fabrication methods are needed.

The advantages of the methods reported here over alternatives are characterized by fine control of sponge features and by the ability to fabricate large, dense Zn sponges with technologically relevant areal-capacity values[5,6,9,10]. Alternative methods to create Zn foams may be unable to create comparable 10 μm pores with sponge porosities near 50%. Such alternatives may, however, require less energy to fabricate because they avoid high-temperature processing steps. Alternative processes include the following strategies: cold sintering Zn particles[11], depositing Zn on three-dimensional host structures[12–17], cutting Zn foil into two-dimensional foams[18], and creating Zn foams via spinodal decomposition[19] or percolation dissolution[20].

The context of the reported methods in the wider body of the published literature is primarily established by work from Drillet et al.[21]. They adapted methods of fabricating porous ceramics to create one of the earliest reported three-dimensional, albeit fragile, Zn foams for batteries. These authors, however, failed to demonstrate rechargeability, likely because of the poor connectivity between the Zn particles. Prior to rechargeable Zn-sponge electrodes, the best alternative to a Zn foil electrode was a Zn-powder electrode, wherein Zn powder is mixed with a gel electrolyte. Zinc-powder electrodes are commercially used in primary alkaline batteries (Zn–$MnO_2$) but have poor rechargeability because Zn particles become passivated by Zn oxide (ZnO), which can increase local current density that spurs dendrite growth[3,22]. We note that there are other dendrite-suppression strategies that do not involve foam or sponge architectures[23,24].

The reported Zn-sponge fabrication methods require a tube furnace, sources of air and nitrogen gas ($N_2$), and a fume hood. All steps can be performed at a lab desk without environmental control, but exhaust from the tube furnace during heat treatment should be piped to a fume hood. Resulting electrodes are appropriate for those interested in creating rechargeable Zn

electrodes capable of high areal capacity (> 10 mAh $cm_{geo}^{-2}$)[6].

The first reported fabrication method is an emulsion-based route to create Zn-sponge electrodes. The second, is an aqueous-based route. An advantage of the emulsion route is its ability to create Zn paste that, when dried, is easy to demold from a mold cavity. A disadvantage is its reliance on expensive materials. For the aqueous route, sponge preforms can be challenging to demold, but this process uses inexpensive and abundant materials.

Both methods involve mixing Zn particles with a porogen and viscosity-enhancing agent. The resulting mixture is heated under $N_2$ and then breathing air (not synthetic air). During heating under $N_2$, the Zn particles anneal and the porogen decomposes; under breathing air, the annealed Zn particles fuse and the porogen burns out. These processes yield metal foams or sponges. The mechanical and electrochemical properties of the Zn sponges can be tuned by varying Zn-to-porogen mass ratio, heating time under $N_2$ and air, and size and shape of the Zn and porogen particles.

**PROTOCOL**

**1. An emulsion-based method to create Zn-sponge electrodes**

1.1 Add 2.054 mL of deionized water to a 100 mL glass beaker.

1.2 Add 4.565 mL of decane to the beaker.

1.3 Stir in 0.1000 ± 0.0003 g of sodium dodecyl sulfate (SDS) until dissolved.

1.4 Stir in 0.0050 ± 0.0003 g of *water-soluble* medium viscosity carboxymethyl cellulose (CMC) sodium salt by hand for 5 min or until the CMC is fully dissolved.

NOTE: Use plastic or plastic-coated stirring tools. Stirring with tools with a metallic surface can adversely affect resulting Zn sponges.

1.5 Stir in 0.844 ± 0.002 g of *water-insoluble* preswollen carboxymethyl cellulose resin.

NOTE: This type of water-insoluble resin is expensive (USD$420 $kg^{-1}$)[6].

1.6 Stir this mixture at 1,000 rpm for 5 min using an overhead paddle stirrer equipped with a plastic paddle.

1.7 Pour 50 g of Zn powder (average particle size of 50 µm, containing 307 ppm of bismuth and 307 ppm of indium for corrosion suppression) into the beaker while the overhead stirrer continues to spin at 1,000 rpm.

1.8 Continue to stir the Zn paste for an additional 5 min at the same rate, 1,000 rpm.

1.9 Stop the stirrer, remove the beaker, and outgas the mixture by placing the beaker and its contents under vacuum for 5 min in a desiccator at room temperature.

1.10 Portion the Zn paste into polypropylene molds (~10 mm in diameter and ~5 mm in height) and let them dry in open air overnight. The shape of the mold dictates the form of the dried paste and resulting Zn sponges.

NOTE: Mold size and shape can vary. Past experiments[5] successfully use cylindrical molds with diameters near 10 mm. Fill the Zn paste up to a height of 5 mm or less. The shorter the height, the shorter the required drying time. See **Table of Materials** for commercially available molds.

1.11 Carefully remove the dried Zn paste preforms from the molds and place them into a mesh casing that rests on a notched alumina holder[5,6].

NOTE: Fabricate mesh casing, for instance, by bending a perforated-brass sheet into a cylinder with a diameter that is slightly larger than the desired diameter of the Zn-sponge electrode. Spray the perforated-metal sheet with boron-nitride lubricant after bending into a desired shape.

1.12 Place the assembly into a tube furnace (67 mm in diameter) with ports to flow gas in and out of the tube.

NOTE: Use one port (the entrance port) to pipe gas into the furnace. Use the other (the exit port) to vent gas out of the tube furnace into a fume hood.

1.13 Pipe $N_2$ gas into the furnace for 30 min at a rate of 5.7 $cm \cdot min^{-1}$ to purge the furnace of air.

NOTE: Step 1.13 can be achieved by connecting a tank of $N_2$ gas with a digitally controlled flow meter to a tube connected to one of the entrance ports. Gas flow meters can be controlled manually or by a computer.

1.14 Throttle the $N_2$ gas to a constant rate of 2.8 $cm \cdot min^{-1}$ after the 30 min purge.

1.15 Program the furnace to increase temperature linearly from 20 to 369 °C over the course of 68 min, hold at 369 °C for 5 h, rise linearly from 369 to 584 °C over the course of 105 min, and then turn off.

1.16 Start the furnace program while the $N_2$ gas continues to flow.

1.17 Manually stop the $N_2$-gas flow after the 5 h temperature hold and pipe in breathing air at 2.8 $cm \cdot min^{-1}$.

NOTE: Step 1.17 can be achieved by connecting a tank of breathing air (not synthetic air) with a digitally controlled flow meter to a tube connected to an additional entrance port.

1.18 Once the heating program stops, let the furnace cool to room temperature without active cooling, but keep the breathing air flowing.

1.19 Remove the cooled Zn sponges and saw them and/or sand them to desired dimensions.

NOTE: A variety of sawing tools can be used such as hand-held rotary saws or vertical band saws. Abrasive or diamond blades are appropriate.

**2. An aqueous-based method to create Zn-sponge electrodes**

2.1 Add 10.5 mL of deionized water to a 100-mL glass beaker.

2.2 Stir in 0.120 ± 0.001 g of *water-soluble* high-viscosity cellulose gum, also known as carboxymethyl cellulose (CMC) sodium salt.

NOTE: Use plastic or plastic-coated stirring tools. Stirring with tools with a metallic surface can adversely affect resulting Zn sponges.

2.3 Vortex and stir this mixture by hand for 5 min or until the CMC is dissolved.

2.4 Stir in 2.400 ± 0.001 g of corn starch while vortexing for an additional 2 min.

2.5 Stir in 120.00 ± 0.01 g of Zn powder (average particle size of 50 µm, containing 307 ppm of bismuth and 307 ppm of indium for corrosion suppression) while vortexing for an additional 2 min.

2.6 Press the resulting Zn paste into desired mold cavities.

NOTE: Mold size and shape can vary. Past experiments[6] successfully use cylindrical molds with diameters near 10 mm. Fill the Zn paste up to a height of 50 mm or less. The aqueous Zn paste is dryer than the emulsion Zn paste, so the aqueous version can be used to make larger sponges that require less drying time. The shorter the height, the shorter the required drying time. The mold needs to be able to split in half as the aqueous Zn paste minimally contracts after drying, unlike the emulsion Zn paste. Unsalted butter can be used to lubricate the molds before pressing in the aqueous Zn paste to aid in demolding. **Figure 1a** shows the custom-machined molds packed with Zn paste following the aqueous-based protocol. **Figure 1b** shows the hand-made mesh casing, notched alumina holder, and resulting Zn sponge made using the aqueous-based method.

2.7 Leave the Zn-paste-filled molds to dry overnight at 70 °C in open air in a furnace.

2.8 Follow the same handling and heat treatment steps (1.11–1.19) described for the emulsion-based method.

## REPRESENTATIVE RESULTS

Resulting, fully heat-treated, emulsion-based Zn sponges have densities of 2.8 $g \cdot cm^{-3}$ while aqueous-based sponges approach 3.3 $g \cdot cm^{-3}$. During heating under air, a layer of ZnO forms on the Zn surfaces, which should have a thickness of 0.5–1.0 µm (observed using scanning electron microscopy)[5]. The solid in the resulting sponges should be 72% Zn (emulsion version) or 78% Zn (aqueous version) with the remainder being ZnO (measured by X-ray diffraction)[6]. Both sponges should have porosities near 50%, pore-diameter distributions centered on 10 µm, and specific surface areas of 4.0 $m^2 \cdot g^{-1}$ (measured via mercury-intrusion porosimetry)[6]. The tensile strength of both sponges should be 1.1–1.2 MPa (measured with diametral compression)[5,6]. We note that the sponges should be rigid and brittle. Cross-sections of the Zn sponges should look similar to those shown in **Figure 2A,B**. If all the properties of the fabricated sponges fall within the provided ranges, the result is positive; if not, the result is negative.

With the stated properties, Zn sponges cycle well in properly constructed batteries. Their performance also depends on the counter electrode, electrolyte, separator, and cell construction; construction of reliable full cells is beyond the scope of this paper. To test the electrochemical validity of Zn sponges, we recommend harvesting commercial counter electrodes from nickel–metal hydride batteries[5,6]. Shape a Zn-sponge to have a 10 mm diameter and 0.5-mm thickness. Cycle this sponge at 20 $mA \cdot cm_{geo}^{-2}$ (geometric area) for discharge and 10 $mA \cdot cm_{geo}^{-2}$ for charge in a nickel–zinc cell as described in the literature[5]. Assuming appropriate construction, the Zn-sponge electrode should show cycling stability at a gravimetric capacity of 328 $mA \cdot h \cdot g_{sponge}^{-1}$ (per gram of ZnO@Zn-sponge electrode) as shown in **Figure 2C**, which maps to 43% depth of discharge (the quotient of gravimetric discharge capacity with respect to every atom of Zn in the electrode divided by the theoretical gravimetric capacity of Zn). After extensive cycling, no dendrites are observed by scanning electron microscopy (**Figure 3**). X-ray diffraction can be used to track the state of charge of the Zn-sponge electrode by monitoring Zn and ZnO reflections[1]. We note the surface of the Zn sponge undergoes restructuring during cycling. The deeper the level of discharge and the greater the cycle life, the greater the amount of restructuring[5]. These factors contribute to the difference in surface morphology shown in **Figure 3A,B**. If this rechargeable capacity is achieved, the result is positive; if not, the result is negative and could be caused by either the Zn sponge, poor cell construction, or failure of other cell components.

**Figure 1: Zinc sponges before and after heat treatment using the aqueous-based method.** (**A**) Photo of custom-machined molds made from Delrin or polyoxymethylene (POM) that is packed with Zn paste before heating occurs. (**B**) Photo of hand-made mesh casing, notched alumina holder, and resulting Zn sponge after heat treatment.

**Figure 2: Zinc-sponge morphology and electrochemical performance.** Scanning electron micrographs of cross-sectioned (**A**) emulsion-based Zn sponge and (**B**) aqueous-based Zn sponge. (**C**) Voltage versus time of an emulsion-based sponge cycled in a nickel–zinc cell discharged at 20 $mA \cdot cm_{geo}^{-2}$ and charged at 10 $mA \cdot cm_{geo}^{-2}$ with a gravimetric capacity of 328 $mA \cdot h \cdot g_{sponge}^{-1}$. Data adapted from Hopkins et al.[5,6].

**Figure 3: Zinc-sponge electrodes suppress dendrite formation.** Emulsion-based Zn sponge (**A**) before and (**B**) after electrochemical cycling. Data adapted from Hopkins et al.[5].

## DISCUSSION

Modifications and troubleshooting associated with these protocols include filling the freshly mixed Zn paste into a mold cavity. Care should be taken to avoid air pockets. Unwanted voids can be decreased by tapping the mold after filling or while filling. Because the aqueous Zn paste is dry, pressure can be applied directly to the Zn paste to push out air pockets while filling up the mold cavity.

A limitation of the methods is that Zn-sponge pore structure is disordered, but the Zn and porogen particle sizes can be used to alter pore morphology. A more ordered and potentially stronger and lighter Zn sponge may be fabricated using additive manufacturing. The mechanical and electrochemical properties of resulting Zn sponges, however, can be tuned by varying Zn-to-porogen mass ratio and the size and shape of the Zn and porogen particles[5,6]. Another potential limitation is that the dried Zn-paste can be fragile, so transferring it into a mesh casing may be challenging and limit Zn-sponge size.

The significance of these methods with respect to existing methods is that resulting Zn sponges achieve long cycle life with high volumetric and areal capacities[5,6]. Resulting Zn sponges are also mechanically robust[5,6].

Future applications of the processes could, in principle, be adapted to create other metal foams for batteries or other applications. For example, iron, magnesium, or aluminum foams may be useful as anodes for metal–air batteries[25,26,27]. Zn-sponge electrodes, in particular, can be used to create batteries for a range of applications that include wearables, grid storage, personal electronics, electric vehicles, and electric aviation[28].

A critical step, which may also require modification or troubleshooting, is the heating process. Furnace temperatures can vary. The heating time under $N_2$, near but below the melting point of Zn, anneals the Zn particles together. The heating time under air burns out the residual porogen, fuses the Zn, and forms a ZnO layer. If the Zn particles appear to be fusing improperly, increase the heating time under $N_2$. If the ZnO layer is too thick, decrease the heating time under air by 10 min or more until the desired thickness of thermal oxide is achieved.

We note that a thick layer of ZnO enhances the mechanical properties of the Zn sponge but also decreases the immediately useable capacity of the Zn electrode. The Zn electrode can be charged by electrochemically converting ZnO to metallic Zn. However, stable cycling at 40% depth of discharge can be achieved without any precharge[5]. If the ZnO layer is too thin, the Zn sponge can crumble during handling[5].

## ACKNOWLEDGMENTS

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## DISCLOSURES

J.F.P., D.R.R., and J.W.L. hold patents related to zinc electrodes: US Patents no. 9802254, 10008711, and 10720635, EU Patent no 2926395, and China Patent no. 104813521.

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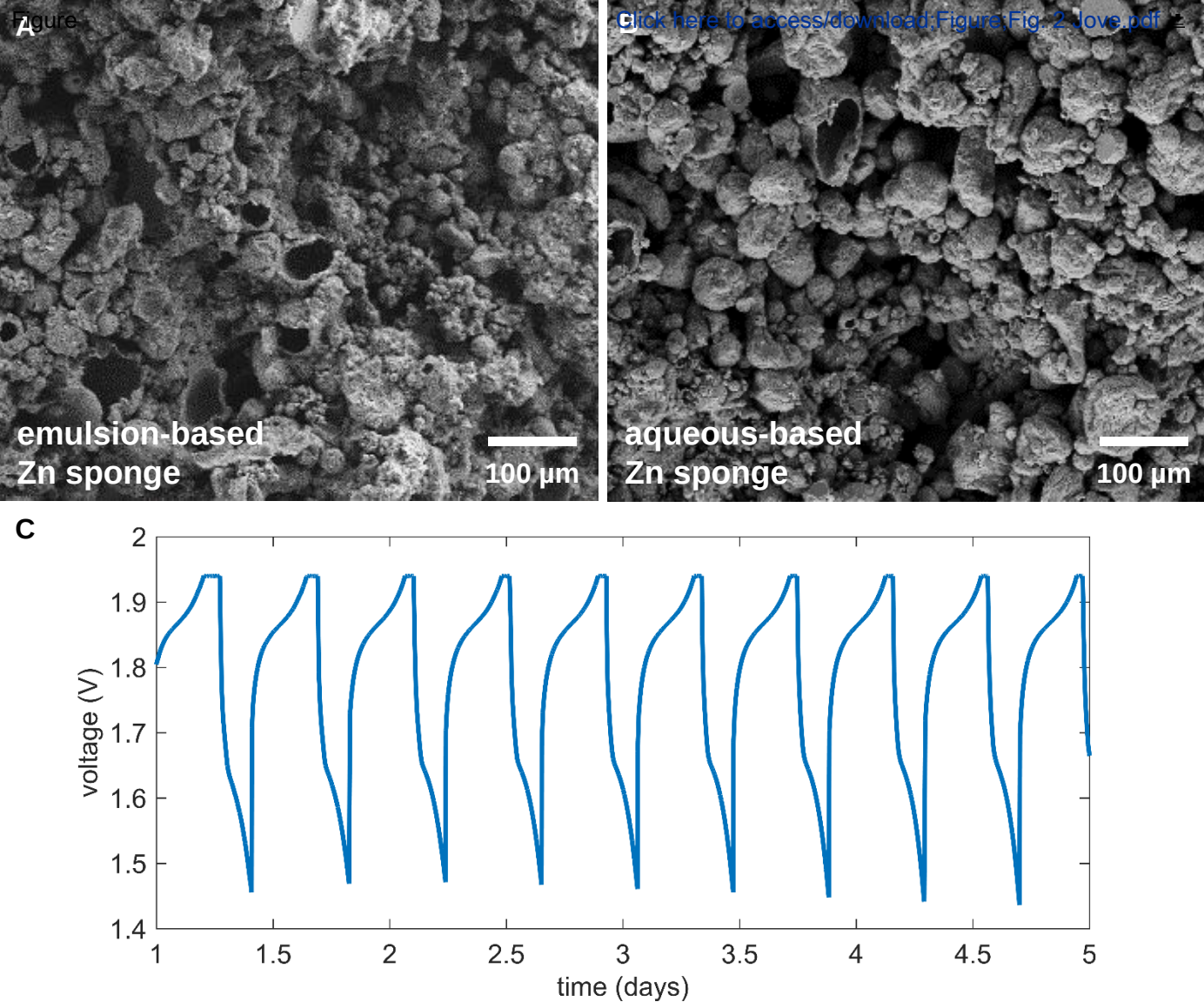
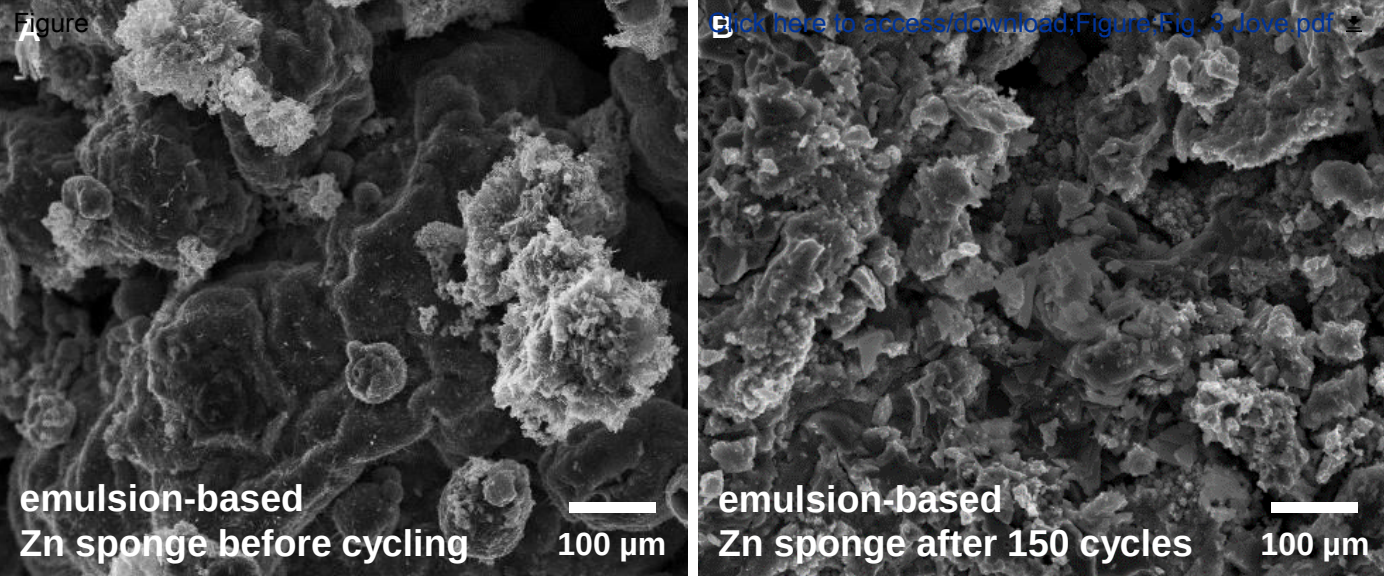
Figure





Figure





| Name of Material/Equipment | Company | Catalog Number | Comments/Description |
|---|---|---|---|
| Corn starch | Argo | Not applicable | This acts as a porogen and viscosity-enhancing agent. |
| Decane | MilliporeSigma | D901 | |
| Medium viscosity water-soluble carboxymethyl cellulose (CMC) sodium salt | MilliporeSigma | C4888-500G | This CMC acts primarily as a viscosity-enhancing agent. |
| Overhead stirrer | Caframo Lab Solutions | BDC3030 | |
| Small cylindrical models for Zn sponges | VWR | 66014-358 | The caps of the vials can be used as molds. |
| Sodium dodecyl sulfate | MilliporeSigma | 436143 | |
| Water-insoluble IonSep CMC 52 preswollen carboxymethyl cellulose resin | BIOpHORETICS | B45019.01 | This CMC acts as a porogen and viscosity-enhancing agent. |
| Zn powder | EverZinc | Custom order | |

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**We have now included more of these details.**

1) 1.10,2.6: Provide mold specifications.

**We now include the following text related to 1.10 and 2.6 respectively:**

**"NOTE: Mold size and shape can vary. Past experiments[5] successfully use cylindrical molds with diameters near 10 mm. Fill the Zn paste up to a height of 5 mm or less. The shorter the height, the shorter the required drying time. See Table of Materials for commercially available molds."**

**"NOTE: Mold size and shape can vary. Past experiments[6] successfully use cylindrical molds with diameters near 10 mm. Fill the Zn paste up to a height of 50 mm or less. The aqueous Zn paste is dryer than the emulsion Zn paste, so the aqueous version can be used to make larger sponges that require less drying time. The shorter the height, the shorter the required drying time. The mold needs to be able to split in half as the aqueous Zn paste minimally contracts after drying, unlike the emulsion-based Zn paste. Unsalted butter can be used to lubricate the molds before pressing in the Zn paste to aid in demolding. Figure 1a shows our custom machined molds packed with Zn paste following the aqueous-based protocol. Figure 1b shows our hand-made mesh casing, notched alumina holder, and resulting Zn sponge made using the aqueous-based method."**

2) 1.13-1.18: How is this done? Is there a manual control or computer control. Please mention specifics such as knob turns or button clicks.

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**"NOTE: Step 1.13 can be achieved by connecting a tank of $N_2$ gas with a digitally controlled flow meter to a tube connected to one of the entrance ports. Gas flow meters can be controlled manually or by a computer."**

**"Program the furnace to increase temperature linearly from 20 to 369 °C over the course of 68 min, hold at 369 °C for 5 h, rise linearly from 369 to 584 °C over the course of 105 min, and then turn off."**

3) 1.19: Mention saw specifications.

**We now include the following text:**

**"NOTE: A variety of sawing tools can be used such as hand-held rotary saws or vertical band saws. Abrasive or diamond blades are appropriate."**

• Protocol Highlight: Please highlight ~2.5 pages or less of text (which includes headings and spaces) in yellow, to identify which steps should be visualized to tell the most cohesive story of your protocol steps.
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2) The highlighted steps should form a cohesive narrative, that is, there must be a logical flow from one highlighted step to the next.
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4) Notes cannot be filmed and should be excluded from highlighting.

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• Figures: Please remove the embedded figures from the manuscript. Figure legends, however, should remain within the manuscript text, directly below the Representative Results text.

**We have removed the figures and kept the figure legends as requested.**

• Table of Materials:
1) Please remove the registered trademark symbols TM/R from the table of reagents/materials.

**Done.**

2) Please sort in alphabetical order.

**Completed.**

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**Noted. None of the figures are exact copies from previous publications. We note if they use previously published data.**

Comments from Peer-Reviewers:

_____

Reviewers' comments:

Reviewer #1:

This work proposes the dendrite protection method of preparing sponge-like Zn anode with a focus on the preparation method. Two different types of methods proposed using emulsion or aqueous solutions. This Zn sponge was examined to show excellent cycling performance even in the alkaline electrolyte. However, some essential data are absent to present the electrochemical details of the novel Zn anode. Thus, I recommend the major revision of this manuscript as follows.

1. The heating under air will inevitably lead to the formation of ZnO, which is thought to influence the electrochemical behavior of Zn sponge. Please discuss this.

**We now include a discussion on this topic in the text:**

**"We note that a thick layer of ZnO enhances the mechanical properties of the Zn sponge but also decreases the immediately useable capacity of the Zn electrode. The Zn electrode can be charged up by electrochemically converting ZnO to metallic Zn. However, stable cycling at 40% depth of discharge can be achieved without any precharge[5]. If the ZnO layer is too thin, the Zn sponge can crumble during handling[5]."**

2. As wrote in the experimental section, the water-insoluble resin is expensive, weakening the advantage of low cost of Zn batteries. So, is it possible to substitute this expensive resin by a low-cost one?

**We were unable to find a commercially available low-cost resin that met our needs after searching for 1.5 y. This is why we created the aqueous-based method that uses inexpensive corn starch as the porogen.**

3. what about the processability of this Zn sponge? Zn batteries are usually used as flexible batteries to power electronics under various mechanical deformations.

**We now note that, "that the sponges should be rigid and brittle." We envision them being used for applications that do not require flexibility such as grid storage. Also, commercial Zn–air batteries are used in hearing aids, which do not require flexibility. We are unaware of any commercial flexible Zn batteries.**

4. The authors are suggested to discuss more about the progress in dendrite protection of Zn anode, and some related works (10.1002/adma.201903778; 10.1002/adma.202001755) regarding the typical protection strategies can be cited to highlight the significance of this work.

**The focus of this manuscript is on Zn sponges or foams. We consequently focus on previous work related to the synthesis of these 3D structures. We agree, however, that it is valuable to highlight some non-foam strategies to suppress dendrites.**

**We now include the suggested references with the following text.**

**"We note that there are other dendrite-suppression strategies that do not involve foam or sponge architectures[23,24]."**

5. It is essential to discuss the pulverization phenomenon of Zn sponge as observed by SEM images in Figure 2.

**The Zn sponge is NOT pulverized when cycled at high depths of discharge for more than 100 cycles. The surface of the Zn becomes textured. The focus of this article is on the Zn-sponge synthesis. For this reason, we do not go into more details here. For more information about the surface restructuring we direct readers to reference 5 (Hopkins, B. J. et al. Fabricating architected zinc electrodes with unprecedented volumetric capacity in rechargeable alkaline cells. *Energy Storage Materials*. 27, 370–376 (2020).)**

**We have now included the following text:**

**"We note that the surface of the sponge undergoes restructuring during cycling. The deeper the level of discharge and the greater the cycle life, the greater the amount of restructuring[5]. These factors contribute to the difference in surface morphology shown in Figure 3a,b."**

Besides, please also check the composition of the Zn sponge after cycling.

**We have reported the X-ray diffraction patterns for 20, 40, 60, and 80% depth-of-discharge (Parker, J. F. et al. Retaining the 3D Framework of Zinc Sponge Anodes upon Deep Discharge in Zn–Air Cells. *ACS Applied Materials & Interfaces*. 6 (22), 19471–19476 (2014).).**

**We mention this in the text:**

**"X-ray diffraction can be used to track the state of charge of the Zn-sponge electrode by monitoring Zn and ZnO reflections[1]."**

Reviewer #2:
The authors provide a complete and concise description of their method to produce zinc sponge anodes via two similar routes using (1) more expensive materials that result in more favorable processing conditions and (2) more economical materials that result in less favorable processing conditions. The manuscript is of overall high quality, fairly clear, and easy to read. Some clarifications or corrections are suggested below:

1. A paragraph in the introduction giving a broad-strokes overview of each of the two fabrication methods would improve this section, since the focus of this journal is on the methods presented.

**We have added the following "broad-strokes" overview paragraph to the introduction:**

**"Both methods involve mixing Zn particles with a porogen and viscosity-enhancing agent. The resulting mixture is heated under $N_2$ and then breathing air (not synthetic air). During heating under $N_2$, the Zn particles anneal and the porogen decomposes; under breathing air, the annealed Zn particles fuse and the porogen burns out. This process yields a metal foam or sponge. The mechanical and electrochemical properties of the Zn sponges can be tuned by varying Zn-to-porogen mass ratio, heating time under $N_2$ and air, and size and shape of the Zn and porogen particles."**

2. Citations are mis-numbered at least in some cases. e.g. Drillet, J.F. et al is numbered 20 in the introduction (line 69) but it is Reference 21 (line 316).

**We have now corrected this error.**

3. Line 92 remove "To create… electrode" (redundant)

**Noted and removed.**

4. Must the liquid volumes be so precise, or can sig. figs. be reduced?

**We wrote the protocol based on what we perform in lab. It is possible that the liquid volume does not need to be so precise. We cannot comment, however, on how a less precise fluid volume will affect the results. Small variations should not affect Zn-sponge outcomes.**

5. Line 121 source of polypropylene molds should be added to the materials/equipment table. Or was this fabricated in house? Note on material and method for this would be helpful, as was done for the mesh casing. A picture of such a mold would also be helpful in the text if it is to be a standalone description of the method.

**We have now included the source for the molds that we purchased. We also included a new figure that is now titled Figure 1, which shows our custom-machined mold for the aqueous protocol.**

6. Line 135 tube furnace diameter is needed, as 1 in vs 4 in would result in quite different gas velocity. Providing manufacturer and product number would be useful for newcomers to the field.

**We now include the tube diameter, "Place the assembly into a tube furnace (67 mm in diameter) with ports to flow gas in and out of the tube."**

**We also changed volumetric flow rates to linear flow rates to avoid ambiguity.**

7. Line 142 a note on why this precise temperature would be welcome, as the goal of JoVE is to cover important and necessary details in methods.

**We wrote the protocol based on what we perform in lab. The reason why the numbers are not multiples of 2 or 5 is because our furnace slowly drifted from its appropriate temperature calibration. The temperature values that we report are the corrected values. Slightly different heating temperatures should not affect Zn-sponge outcomes.**

8. Line 152 providing manufacturer and product number or description for diamond saw might be useful.

**We have used a variety of diamond saws and more common abrasive saws to cut the Zn sponges. Special cutting tools are not required. We now clarify this issues with the following statement:**

**"A variety of sawing tools can be used such as hand-held rotary saws or vertical band saws. Abrasive or diamond blades are appropriate."**

9. For route 2 (aqueous) it would be useful to again specify target mass or volume of Zn paste since it is different from the target of route 1.

**We do not specify target masses or volumes for resulting sponges because different applications may require electrodes with different diameters, heights, or areal capacities. We do specify that, "[r]esulting, fully heat-treated, emulsion-based Zn sponges have densities of 2.8 g $cm^{-3}$ while aqueous-based sponges near 3.3 g $cm^{-3}$."**

10. Line 250 is any thermal oxide desired? Would the experimentalist do well to minimize the formation of thermal oxide? One would think so, since charging Zn sponge anode opposite fully charged cathode would require OER to take place on cathode, which is undesirable in the full cell.

**We clarify this issue with the following text:**

**"We note that a thick layer of ZnO enhances the mechanical properties of the Zn sponge but also decreases the immediately useable capacity of the Zn electrode. The Zn electrode can be charged up by electrochemically converting ZnO to metallic Zn. However, stable cycling at 40% depth of discharge can be achieved without any precharge[5]. If the ZnO layer is too thin, the Zn sponge can crumble during handling[5]."**

Reviewer #3:
Manuscript Summary:
The paper reports two methods to fabricate porous zinc sponge electrodes for Zn-based batteries. Both methods are argued to have the up-scaling capability with tailored porosity, pore structure, and pore size. The Zn electrodes produced through these methods are shown to suppress shape change and dendrites formation during battery cycling.

Major Concerns:
Adding a sentence on whether additional care is needed concerning the experimental part would be useful. For example, does the annealing step release any gases that need a proper ventilation? Besides, i assume that the work (like paste formation) could be carried out in a lab desk without the need for a fume hood.

**We clarify this issue with the follow text clarification:**

**"The reported Zn-sponge fabrication methods require a tube furnace, sources of air and nitrogen gas ($N_2$), and a fume hood. All steps can be performed at a lab desk without environmental control, but exhaust from the tube furnace during heat treatment should be piped to a fume hood."**

Minor Concerns:
line 105: adding the price would be helpful step

**We clarify this issue with this text:**

**"NOTE: This type of water-insoluble resin is expensive (420 USD $kg^{-1}$)[6]."**

1.16: is it synthetic air or just compressed air?

**We clarify this issue with this text:**

**"This mixture is heated under $N_2$ and then breathing air (not synthetic air)."**

step 1.18: still with the air flow until the temperature is cooled down?

**We clarify this issue with this text:**

**"After reaching 584 °C, shut off the furnace, let it cool to room temperature without active cooling, but keep the breathing air flowing."**

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6 August 2020

Dr. Ronald Myers
Director of Editorial, Journal of Visualized Experiments
<www.jove.com>

Dear Dr. Myers,

In response to Benjamin Werth's invitation, we present our revised manuscript (JoVE61770), "Zinc-sponge battery electrodes that suppress dendrites," to *Journal of Visualized Experiments*. We added a new figure and clarifying text based on the reviewers' recommendations. Due to software limitations, we are unable to provide vector-image files, so we have uploaded PDF images as outlined in the instructions for authors. We included a point-by-point response to the reviewers' questions and comments. We also uploaded one manuscript with all tracked changes along with a clean PDF version. Thank you for your consideration.

Sincerely,

Debra R. Rolison

Debra R. Rolison, Ph. D.
Advanced Electrochemical Materials Section, Head

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| Author(s): | Brandon J. Hopkins, Megan B. Sassin, Joseph F. Parker, Jeffrey W. Long, Debra R. Rolison |

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