• Protocol Detail: Please note that your protocol will be used to generate the script for the video, and must contain everything that you would like shown in the video. Please add more specific details (e.g. button clicks for software actions, numerical values for settings, etc) to your protocol steps. There should be enough detail in each step to supplement the actions seen in the video so that viewers can easily replicate the protocol.

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.

We now include the following text:

"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.
1) The highlighting must include all relevant details that are required to perform the step. For example, if step 2.5 is highlighted for filming and the details of how to perform the step are given in steps 2.5.1 and 2.5.2, then the sub-steps where the details are provided must be included in the highlighting.
2) The highlighted steps should form a cohesive narrative, that is, there must be a logical flow from one highlighted step to the next.
3) Please highlight complete sentences (not parts of sentences). Include sub-headings and spaces when calculating the final highlighted length.
4) Notes cannot be filmed and should be excluded from highlighting.

We have now added highlighting.

• Discussion: JoVE articles are focused on the methods and the protocol, thus the discussion should be similarly focused. Please ensure that the discussion covers the following in detail and in paragraph form (3-6 paragraphs): 1) modifications and troubleshooting, 2) limitations of the technique, 3) significance with respect to existing methods, 4) future applications and 5) critical steps within the protocol.

We now explicitly follow this language and order in the discussion section.

• 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.

• If your figures and tables are original and not published previously or you have already obtained figure permissions, please ignore this comment. If you are re-using figures from a previous publication, you must obtain explicit permission to re-use the figure from the previous publisher (this can be in the form of a letter from an editor or a link to the editorial policies that allows you to re-publish the figure). Please upload the text of the re-print permission (may be copied and pasted from an email/website) as a Word document to the Editorial Manager site in the "Supplemental files (as requested by JoVE)" section. Please also cite the figure appropriately in the figure legend, i.e. "This figure has been modified from [citation]."

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."