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Vertically integrated high voltage Zn-Air batteries enabled by stacked multilayer electrodeposition



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HIGHLIGHTS

• This paper reports a scheme for serially connected zinc-air battery stacks.

• Fabrication is achieved through a sequential multilayer and stacking approach.

• Scalable battery output voltages were obtained with minimal resistive loss.

• Volumetric energy densities of up to 1720 WhL⁻¹ are demonstrated.

A R T I C L E I N F O A B S T R A C T Keywords: We report a scheme for the integrated fabrication of MEMS-scale, series-connected battery cells. The approach exploits multilayer electrodeposition of active and sacrificial layers to generate structures that can be formed into high voltage power sources. Aqueous, non-vacuum-based fabrication, via electrodeposition, enables high throughput and deterministic control of layer thicknesses and battery performance. Batteries manufactured using this technique offer the potential to match supply voltages to system needs, ranging from conventional electorements.

tronics to direct drive of high voltage electrostatic or piezoelectric MEMS.

1. Introduction

In the last 15–20 years as the concept of the Internet of Things (IoT) has grown, advancements in micro-electromechanical systems (MEMS) sensor and actuation technologies have outpaced developments in micro-scale power source technology. As a result, the footprint area, volume, or weight of the energy storage devices needed to power the next wave of MEMS devices often becomes the limiting factor to realize increased performance efficiency and manufacturing scalability. Subsequently, an area of research need exists in the exploration of fabrication technologies that can generate power supplies that have excellent volumetric energy and power density, a scalable architecture in all three dimensions, and tunable current and/or output voltages. MEMS fabrication techniques such as photolithography, multilayer electrodeposition, and top down laser micromachining and layer stacking have been demonstrated to achieve those goals in the context of high current lithium-ion micro-batteries [1], but design of micro-batteries with tunable and/or scalable output voltages is also critical. The reason that

the development of high voltage micro-batteries is crucial to the IoT universe is that the power and electrical requirements of the MEMS based sensing or actuation devices often vary from those of typical circuitry. In these cases, energy storage devices that provide high and/or multiple voltage levels could eliminate the need for up-conversion technologies typically required to operate the electrostatic or piezoelectric mechanisms used to drive the resulting activity [2,3]. Conventional high voltage batteries utilized in consumer electronics or in larger scale packages like electric cars can be manufactured through external wiring of individual cylindrical battery cells together parallel modules to increase capacity/current output, and then those modules are stacked in series to increase the total output voltage [4]. This serial wiring method enables the voltage and current outputs needed to drive a macro-scale device like an electric car motor. However, translating this approach to smaller scale applications is electrically challenging and reduces specific performance by increasing the electrochemically dead weight to the system [5]. The excess wiring (and packaging to ensure the safety of that wiring) absorbs a much higher fraction of the device volume when

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Fig. 1. Schematic for the self-assembly method of fabrication for stacked, serially connected zinc-air batteries.

the individual cells are scaled down in size. Conversely, the current state-of-the-art micro-batteries can produce high current output and excellent power/energy densities but cannot be scaled or stacked efficiently to achieve the required voltage for many applications [6,7]. Thus, new fabrication approaches are needed to generate serially connected cells (enabling higher voltage outputs) while maintaining intrinsic energy and power density.

MEMS fabrication techniques centered around multilayer electrodeposition can offer an avenue to stacked microstructures that display excellent electrical and ionic transport characteristics [2]. Utilizing these techniques with metal-air battery chemistries for high voltage micro-battery applications is ideal, as they have the potential to achieve high energy densities in a small footprint platform [8,9]. Using air as the cathode active material in these systems enables a low overall mass density and thus the potential for a high-performance battery architecture. Within the metal-air category, there are a number of different potential application chemistries. Lithium, iron, zinc, magnesium, aluminum, and sodium are the typical anode metals used in these configurations [10,11]. Zinc-air chemistry is an ideal fit for multilayer MEMS based micro-batteries since 1) it is compatible with electrodeposition and other aqueous, atmospheric fabrication techniques 2) it is compatible with all types of battery architectures, and 3) zinc has a high theoretical capacity of 820 mAhg⁻¹. Thus, it was chosen as the demonstration vehicle for this study.

Zinc-air primary battery chemistries typically operate with a cell consisting of a pure zinc anode, an alkaline electrolyte, and a porous cathode layer [12]. The cathode layer allows air to diffuse through the cell and enables the oxygen reduction reaction (ORR) at the interface between oxygen and the electrolyte, usually in the presence of a catalyst. The reactions at both electrodes, and overall, are given in Equations (1)–(3).

Cathode:
$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$
 (1)

Anode: $2Zn + 4OH^- \rightarrow 2ZnO + 2H_2O + 4e^-$ (2)

Overall:
$$2Zn + O_2 \rightarrow 2ZnO$$
 (3)

During the discharge of a primary zinc battery, the main limitations on the total power output come from oxygen diffusion through the porous cathode material as well as build-up of zinc oxide product on the anode side that reduces the accessible surface area of zinc to the electrolyte for reaction [13]. Additionally, if the catalyst is poor the kinetics of the ORR can be curtailed, which adds an internal resistance to the cell that manifests in a lower voltage output during operation [13]. Typically, in the earlier portion of the discharge process the resistance due to limitations at the cathode is higher, but the anode becomes rate-limiting toward the end due to the excess zinc oxide. Thus, it is crucial to consider the geometry of both electrodes when designing integrated, full-cell zinc-air batteries.

Various approaches have been utilized in the literature to mitigate some of the issues listed above. These approaches include nanostructuring the zinc anode by using fine powders, ribbons, or fibrous structures [14–17], or by patterning the electrode into deterministic posts or sheets [18–21]. However, these processes are not conducive to integration into a stacked, multi-cell battery that can scale the voltage. Conversely, many reports have investigated catalyst materials that can reduce the charge transfer resistance due to slow ORR kinetics [22–27], but these materials may be challenging to integrate into a layered, multi-cell micro-battery configuration. Thus, this work focuses on the design of a fabrication approach that can effectively generate zinc-air micro-batteries with the following characteristics:

- 1) They are compatible with aqueous, low temperature, atmospheric processing
- 2) They are modular such that a deterministic number of cells can be internally serially connected to achieve scalable voltages without external packaging and without compromising volumetric scalability in any direction
- 3) They do not sacrifice individual cell energy or power density

In this work, a microfabrication approach based on MEMS electrodeposition techniques is presented. This approach has advantages that pertain to the three goals of the high voltage micro-battery outcome that are demonstrated via structural and electrochemical characterization. Sample discharge curves are presented, and the performance metrics of voltage output, total power output, and energy densities are evaluated in conjunction with where these devices fit into the larger energy storage landscape for MEMS actuation and micro-robotic systems.

2. Fabrication approach

An approach based on MEMS fabrication techniques is utilized to generate serially connected zinc-air cells. Scaling of the micro-battery is enabled in the z-direction by in-situ series connection of individual cells within an overall battery stack. The series connection is provided by a bipolar current collector, which consists of a metal that connects the cathode of the previous cell to the anode of the next cell in the stack. It is labeled bi-polar because each end of the current collector will have a potential bias of the opposite sign. Additionally, a gel state electrolyte is utilized to minimize the need for packaging. While gel electrolytes can exhibit lower ionic conductivities that can lead to increased internal resistance within each cell, in this case the overall volume and weight minimization (due to limited packaging needs) compensates for the slower transport. Incorporating an integrated series connection, all solid-state materials, and fabrication techniques that enable volume scaling in the z-direction (with thin individual layers) results in excellent specific performance as well as the ability to increase overall battery voltage in multiples of the individual cell outputs. The process is outlined schematically in Fig. 1.

In the first step, a photoresist mold is prepared on a substrate coated with a lift off resist (LOR-3A, MicroChem) and a sputtered seed layer of titanium-zinc. A photoresist mold outlines the footprint area for the ultimate battery, and can be in any shape, although circular is preferred to assist with later fabrication steps. Next, a single set of zinc anode, nickel current collector, and porous gold cathode are sequentially electroplated through the resist mold. After plating, the mold is removed and the individual rings, which consist of the four-layer electrode sets, are mechanically separated from the substrate at the interface of the bottom titanium-zinc layers and the LOR-3A lift off resist. The mechanical separation is initiated by a thin blade and then completed by carefully peeling off from the substrate with tweezers. The isolation of the electrodeposited layers from the substrate is possible due to the difference in adhesion strength of the resist to the substrate compared to the metal pairs. Once separated from the substrate, the free-standing multilayer sets are assembled together in three steps to form a battery stack. First, the cells are arranged on a thin wire coated with enamel, making sure that each set is oriented such that the zinc and gold layers face in the same direction. Next, the rings are dipped into a bath of diluted hydrofluoric acid (0.05 M) to dissolve the thin seed laver of titanium, revealing the zinc surface. Lastly, the rings are coated with a solution of poly(vinyl alcohol), potassium hydroxide, and DI water. This solution is a precursor to what will eventually become the gel electrolyte. The volume of coated gel precursor is optimized to ultimately result in an appropriately thick electrolyte layer for battery operation. After assembly is completed, the stack is placed in a vacuum oven at 400 torr for 20 min. The vacuum drying removes water content and gels the electrolyte, converting it into a semi-solid state. After the vacuum oven treatment, electrical contacts are made to the top and bottom anode/ cathode layers and the final stack is prepared for electrochemical testing.

The foremost benefit of the assembly process is that there are no limitations on the lateral or vertical dimensions of the final multilayer stacked battery. The only lithography step defines the footprint area, which can be easily adjusted by changing the mask dimensions. The total height, total number of cells, and thus the voltage output is determined by how many sets of electrode layers are added to the wire for assembly. The viscosity of the electrolyte solution, the potassium hydroxide concentration, and the pressure at which drying occurs can all impact the final thickness.



Fig. 2. A diagram of porous metal electrodeposition through a polystyrene particle mold.

2.1. Deposition methods and process conditions

2.1.1. Zinc anode electrodeposition

There are a number of different electrodeposition baths utilized in the literature to generate thin zinc films [28–32]. In this case, the most important characteristics of the zinc deposition process are that the solution is compatible with the other materials in the device and that the plated zinc is uniform in thickness such that the structure of subsequent layers is not warped. As a result, an electrodeposition bath consisting of 35 g L⁻¹ zinc sulfate heptahydrate and 80 g L⁻¹ sodium sulfate is utilized. This bath has a neutral pH, has a non-reactive supporting electrolyte and has been shown to be compatible with subsequent active metal depositions such as copper or nickel [33].

Traditionally, a problem with zinc electrodeposition is that the resulting films can be highly dendritic. In this case, slight cracks or pores within the film caused by these dendrites can help performance, as they provide spaces for zinc oxide product to deposit without covering other potential active zinc reaction sites. Thus, a plating current density of 10 mAcm⁻² is utilized.

2.1.2. Cathode fabrication

On the cathode side, there are a number of different electrode and catalyst combinations that have been effective in hosting the oxygen reduction reaction [22–27]. The most common of these pairings is a carbon electrode loaded with platinum catalyst due to its activity for the ORR [34,35]; however, it is difficult to incorporate carbon into the sequential electrodeposition technique described above, and the loading of platinum would require an extra (expensive) step. Thus, gold is used as an alternative material that can accomplish both tasks of conducting current and acting as a catalyst for the reaction.

In order to incorporate pores into the plated gold cathode, a sacrificial mold of polystyrene particles is spray coated on top of the nickel before gold electrodeposition. This method, adopted from Refs. [36,37], has been utilized to create high surface area metal electrodes for other types of micro-batteries. In this case, an airbrush spray gun is used to hold a suspension of 1 μ m polystyrene particles in water, which are spray coated at a distance of 10 cm above the sample surface and at a speed of approximately 2 cm s⁻¹. Five passes over the sample generates a film of particles approximately 5–7 μ m in height, if the water is allowed to evaporate after each pass. Once the particles have packed, they are



Fig. 3. Characterization of a 5 μ m electrodeposited zinc film with a 15 μ m gel electrolyte and a 400 μ m commercial porous carbon/platinum cathode: a) Open circuit potential and b) 0.2C discharge curve.

sintered on a hot plate at 105 °C for two hours. Sintering the particles creates continuous, interconnected paths that become passages for oxygen diffusion during the discharge of the batteries. A schematic of the porous cathode layers and its connection to the nickel current collector is shown in Fig. 2.

After all layers have been plated, the sintered polystyrene particles can be dissolved in toluene, which is a selective etch for the polymer and does not attack any of the metals in the structure. Thus, the porous gold cathode catalyst can be revealed.

2.1.3. Nickel electroless deposition

In this cell assembly approach, the nickel current collector is deposited directly on the zinc anode layer. Thus, careful consideration is needed to ensure that the zinc is not etched or otherwise altered during the deposition. Thus, a neutral pH electroless plating bath is used with a composition based on ions of a nickel complex and hypophosphite together in solution with a catalytic accelerator and a stabilizer [38]. Electroless plating ensures a conformal coating without harming the zinc active material surface. Temperature control is vital to the uniformity of the deposited nickel, and thus the bath is kept between 93 °C and 98 °C during deposition.

2.1.4. Gel electrolyte formation

The gel electrolyte used for both fabrication schemes consists of a mixture of poly(vinyl alcohol), potassium hydroxide, and DI water. To make the gel precursor, 1 g of poly(vinyl alcohol) (MW 88000–98000, 90% hydrolyzed, Aldrich) is mixed with 10 mL of water. The mixture is heated at 85 °C and stirred vigorously for 3–4 h until the polymer has completely dissolved. Separately, a solution of 10 mL of 1 M potassium hydroxide is prepared. Once the poly(vinyl alcohol) solution has dissolved and cooled to room temperature, the two solutions are mixed together and stirred slowly until well mixed. This is the gel precursor solution, which is used in the cell stacking process. The precursor is placed in a vacuum oven at 400 torr and 27 °C for 20 min to complete the gelling process. Due to the reduced water content, the concentration of potassium hydroxide within the gelled electrolyte is increased to a level that provides sufficient ionic conductivity for transport during discharge.



Fig. 4. Chart of oxygen depletion distance in the porous gold cathode as a function of discharge C rate



Fig. 5. Optical and SEM images of the multilayer deposition. a) Wafer after the first zinc layer is plated. b) Wafer after the bi-polar nickel current collector is deposited. c) Wafer after polystyrene spray coat, gold electrodeposition, and photoresist mold removal d) A FIB/SEM cross section of a sample zinc anode, nickel current collector, and gold cathode interface e) A top-down SEM image of the porous gold cathode after polystyrene mold removal

3. Material properties and cell modeling

3.1. Material properties

In order to confirm that the use of sulfate based electroplated zinc does not alter the energy storage capabilities as compared to zinc particles or commercial foils, single cell discharge experiments were performed. These experiments were conducted with a planar geometry, in which electroplated zinc was covered with a uniform layer of gel electrolyte, on top of which a platinum loaded commercial carbon cathode was attached.

The planar sheet geometry enabled direct testing of the zinc utilization without any diffusion constraints, and an excess amount of gel was deposited to ensure complete uptake of the reaction products. Sample open circuit potential and discharge curves of these basic cells are shown in Fig. 3.

In Fig. 4a, the open circuit potential was measured to be 1.6 V, which is very close to the nominal 1.65 V voltage calculated from the thermodynamics. Upon discharge at 0.2C, the plateau voltage was approximately 1.25 V, which is in line with commercial zinc-air batteries. More importantly the zinc utilization was 77%, which is at the higher end of what is seen in state-of-the-art zinc-air batteries in the literature [31]. In general, it is typical to see 60–80% zinc utilization (instead of 100%) due to the zinc oxide reaction products blocking access to unreacted zinc in the structure. This is especially true for film or foil-based electrodes [31]. The results of these experiments provided confidence that electroplated zinc could be incorporated into the proposed micro-batteries.

3.2. Cell modeling

In order to optimize the geometries of the full cells fabricated using MEMS techniques as described above, a model was built to assess the diffusion and reaction limitations of oxygen at the cathode and zinc at the anode. Given excellent contact between the gel and electrodes as well as high ionic conductivity in the gel electrolyte, the power capability is determined by the rate at which oxygen can be supplied to the interface of the cathode catalyst and electrolyte.

The model employed in this work is adopted from previous work in our groups [39]. A mass balance around the cathode is used to determine the oxygen concentration through the porous cathode as a function of the porosity, diffusion coefficient and discharge rate (which is proportional to the rate of oxygen reduction reaction at the surfaces). The governing equations of the oxygen transport are listed in Equations (5)– (7).

$$D_{o_2}\frac{\partial^2 C_{o_2}}{\partial x^2} + \dot{q} = 0 \tag{5}$$

$$\dot{q} = \frac{\left(P/\#cell\right)}{V_p * F * V_{O2,cath}} \tag{6}$$

$$C_{O_2} = -\frac{\dot{q}}{2D_{O_{2,e}}\varepsilon_{void}^{1.5}}x^2 + \frac{\dot{q}L_c}{D_{O_{2,e}}\varepsilon_{void}^{1.5}}x + C_{O_2}^0$$
(7)

In Equation (5), D_{02} is the diffusion coefficient of oxygen in air, C_{02} is the concentration of oxygen, which is calculated as a function of the distance x into the depth of the battery from any edge. \dot{q} , as described in Equation (6), is the flux of oxygen that is removed from the porous cathode due to the ORR. The magnitude of this flux is dependent on the power drawn from the stack, P, the number of cells, the plateau voltage during discharge, V_p, Faraday's constant, F, and the volume of oxygen in the pores of the cathode, $V_{\text{O2,cath.}}$ The power divided by the discharge voltage gives the current, so this part of the expression essentially represents the current, or C rate of discharge. The larger this number is, the faster the oxygen will be reacted and removed from the cathode. Solving the continuity equation reveals Equation (7), which is the expression for the oxygen concentration at any position within the cathode. Setting the concentration to zero and solving for x gives an expression for the location within the cell that the oxygen concentration drops to zero, as a function of q, D_{O2} , and ε_{void} , which is the porosity of the cathode. This expression is listed as Equation (8).

$$L_{dep} = \sqrt{\frac{2C_{O_2}^0 D_{O_2} \varepsilon_{void}^{1.5}}{\dot{q}}}$$
(8)

As seen in the Fig. 4 inset, oxygen enters the cathode from the edge of the cell and diffuses through the continuous porous paths generated by gold electrodeposition through packed polystyrene particles. If the particles are assumed to have packed in an FCC structure, the porosity of the gold cathode film can be estimated at 80% [40]. Equation (8) can then be used to calculate the oxygen depletion distance, L_{dep}, as a function of the oxygen flux, which is proportional to the C rate. If the depletion distance is less than half of the characteristic cell length for a given C rate, this indicates that the zinc past that point will not be utilized, as there is no oxygen to participate in the electrochemical reaction. This set of modeling equations does assume a constant flux of oxygen due to reaction and a mostly diffusion limited regime, but these assumptions are reasonable for gaining a conceptual understanding of the limits of the discharge rates for these zinc-air micro-batteries. The data in Fig. 4 shows the dependence of the oxygen depletion distance on the C rate of discharge.

At a 0.1C discharge rate the depletion distance is just above 0.7 cm, which means that a battery with a 1 cm \times 1 cm footprint area still has all the zinc accessible to react (since the oxygen can diffuse from both sides); however, increasing the rate slightly to 0.4C drops the depletion distance below the cutoff point for a 1 cm battery, and increasing to 1C drops it just below the limit for a 5 mm battery. Decreasing the footprint area further is certainly possible with the lithographic techniques available, but cell alignment and stacking becomes more challenging at that point. Additionally, overall energy output is decreased by continuously decreasing the overall volume of the cells. Thus, the model predicts that either the discharge rate needs to be kept below 1C, or alternative paths for oxygen diffusion need to be built into the battery stack. This is an essential step in the assembly process, as an internal air hole can be used for both aligning battery cells and providing another oxygen diffusion pathway during discharge.

4. Results and discussion

4.1. Structural characterization

Proof-of-concept zinc-air micro-batteries were fabricated using the process outlined above. Structural characterization was completed using optical (Keyence) and scanning electron microscopy (Quanta E-SEM 600), and electrochemical assessment was carried out with a potentio-stat using galvanostatic discharge and cyclic amperometry (Gamry Reference 600+). Fig. 5 shows optical and SEM images of the wafer-level electrodeposition after each of the multilayer steps. In the pattern, multiple geometries were included for characterization of the electrodeposition plating rates as well as the ease of assembly and stacking.

Fig. 5a shows an optical image of the wafer-level pattern after the zinc anode layer is electrodeposited on top of the seed layer. Next, in Fig. 5b, the wafer after nickel electroless plating is shown. Lastly, in Fig. 5c, the wafer after polystyrene spray coating, gold electrodeposition, and photoresist mold removal is shown. It can be seen from these images that the wafer-level uniformity of the plating is good although the surfaces are matte, indicating that there is some surface roughness. This level of roughness does not impact the assembly process, and thus is not concerning as a potential impact on performance of the cells.

In Fig. 5d, uniform interfaces can be identified between thin electroplated layers of the zinc anode, nickel current collector, and porous gold cathode. The zinc layer shows cracks as a result of dendritic growth and the stress of the nickel layer plated on top, but these are actually beneficial to the performance as long as the layers do not detach. The cracks and/or pores provide avenues for zinc oxide deposition that does not completely shut off further zinc metal from reacting. Fig. 5e shows the porous gold cathode. Introduction of randomness in the packing due



Fig. 6. Performance measurements for a single cell: a) Open circuit potential for a sample single cell measurement obtained from manual assembly of two multilayer sets with the poly(vinyl alcohol)/potassium hydroxide gel electrolyte. The inset schematic shows the architecture of the device tested. b) A 0.4C discharge curve for the single cell.

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Parameter	Value	Unit
Footprint area Volume	0.785 1.65 × 10 ⁻³	cm ² cm ³
Discharge C rate	0.4	C
Capacity	1.2	mAh
Power Supplied	1.28	mW
Power Density	787	WL^{-1}
Energy Density	985	WhL^{-1}

to the multiple pass spray coating reduces the overall porosity, but there are still ample avenues for oxygen transport throughout the film.

4.2. Electrochemical performance characterization

For the assembled zinc-air battery stacks, open circuit potential, galvanostatic discharge, and cyclic amperometry techniques were utilized for electrochemical characterization. Single cells were fabricated to assess the effect of optimized geometries based on the diffusion modeling, and a four-cell stack was fabricated to characterize the voltage scaling capabilities. Fig. 6 shows the open circuit potential for the single cell zinc-air battery formed by the multilayer plating and manual assembly procedure, as well as a sample discharge curve at 0.4C.

The OCP measurement of 1.57 V corresponds within experimental error to the 1.65 V nominal value for a zinc-air cell. Thus, it was confirmed that the manual assembly prevents overflow of electrolyte around the boundaries of the stack, and further discharge



Fig. 7. Power performance for a single cell zinc-air micro-battery: a) I-V curve and b) Output power as a function of current density.



Fig. 8. a) Open circuit potential of four-cell zinc-air battery stack fabricated by multilayer electrodeposition and manual assembly. b) 0.2C discharge curve of a four-cell zinc-air battery stack fabricated by multilayer electrodeposition and manual assembly.

characterization was performed. The discharge plateau of 1.28 V matches the discharge of a typical commercial zinc-air device [41]. Given that output voltage and the discharge current of 1 mA, the capacity, energy density, and power density can be calculated, and are summarized in Table 1.

The volumetric power and energy densities listed in Table 1 are based on the total volume of the two-layer sets required to test a single

cell in this configuration. Therefore, if only the middle cell volume is considered (the zinc-gel-gold cell that is undergoing discharge), the volumetric energy and power densities would be 1725 WhL⁻¹ and 1380 W L⁻¹, respectively. These values are very promising for zinc-air cells and indicated the efficacy of the stacked assembly approach [41]. The center hole performs the dual function of facilitating the stacking of individual cells to create a high voltage battery while providing a low resistance diffusion pathway for oxygen to the center of the stack. According to the model developed above, there are no local zones of zero oxygen concentration when the stack is configured this way, and thus when combined with the full gel coating the zinc utilization rises to about 60%. This is standard for commercial zinc-air cells [31].

In order to find the maximum power capabilities of a single cell architecture, the I-V relationship was traced out using galvano-dynamic tests, with the resulting curves plotted in Fig. 7.

In Fig. 7a the cell potential is displayed as a function of the current density used during discharge. The relationship is mostly linear, and results in a peak power output at a discharge current density of 4.7 mAcm^{-2} , as seen in Fig. 7b. The linear I-V curve indicates that there is not an oxygen diffusion limitation in the cells, but rather an ohmic resistance in the electrolyte that dominates. Thus, the optimized cell geometry and use of a porous gold cathode were successful in removing oxygen diffusion and reaction rates as a limiting factor in power generation.

The peak power measured for a single cell is found to be 4.13 mW, which can be scaled by adding more cells to the stack and increasing voltage. While the single cell data is important to understanding the intrinsic performance of these devices, the ultimate goal is to provide direct drive opportunities for piezoelectric or electrostatic MEMS systems. Thus, it is important to highlight the voltage scaling capabilities of these stacked multilayer electrodes with bipolar nickel series connection. As a proof-of-concept device, a four-cell stack was fabricated and tested. The open circuit potential and discharge performance are shown in Fig. 8.

In Fig. 8a, the open circuit potential reading for the four-cell stack is 6.2 V, which corresponds to about 1.55 V per cell. This is slightly lower but within experimental tolerance for the nominal voltage for each cell in the stack, and more importantly it signifies that the bi-polar current collector approach is functional.

During the discharge experiment, shown in Fig. 8b, the end of the open circuit potential measurement is completed before applying a constant current load for the battery discharge. A plateau voltage of 5.1 V is achieved, which corresponds to, on average, 1.3 V per cell. This is very similar to the voltage profiles seen during discharge of the single cell mentioned previously, indicating minimal internal losses as a result of adding more cells to the stack. The power and energy performance of

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Table 2

Summary of multi-cell zinc-air battery stack discharge data.

Parameter	Value	Unit
Footprint area	0.785	cm ²
Number of Cells	4	#
Volume	0.007	cm ³
Discharge C rate	0.2	С
Discharge current density	1.33	mAcm ⁻²
Capacity	2.26	mAh
Zinc utilization	52	%
Power supplied	5.1	mW
Energy Density	1720	WhL^{-1}
Power Density	760	WL^{-1}

the multi-cell stack is summarized in Table 2.

The energy density of the multi-cell stack was greater than that of the single cell due to the smaller fraction of excess, non-reaction hosting layers taking up the volume. The power performance is the same, but this is likely just due to the fact that these cells were operating at a current density away from the peak power number. This was to ensure that, upon discharge, all of the cells within the stack were discharging equally. If one cell within the stack is depleted before the others, a large internal resistance will be located at the site of that cell and could derail the discharge of the battery. In the end, the performance of the stacked zinc-air micro-battery demonstrates that voltage can be scaled through a bi-polar current collector and that excellent energy density metrics can still be maintained.

5. Conclusions

In this work micro-batteries were fabricated with scalable voltage by combining a high energy density zinc-air chemistry with in-situ, bi-polar nickel current collector and an electrodeposited porous gold cathode. All electrode layers are processed in aqueous solutions at room temperature, which increases the manufacturability of the process and the lateral and vertical dimensions of the cell stacks are independently controllable, which enhances the potential application versatility of the energy storage systems. The output voltage of the batteries was scaled at 1.3 V per cell and demonstrated minimal resistive loss at multi cell stacks generating over 5 V. Additionally, high energy densities of up to 1720 WhL⁻¹ were shown. Thus, this fabrication approach shows great promise to generate micro batteries with excellent specific performance that can be integrated with different types of microsystem platforms.

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