High-Energy-Density Zinc–Air Microbatteries with Lean PVA–KOH–K₂CO₃ Gel Electrolytes

Jingwen Zhang,* Yanghang Huang, Qi Yang, Vishal Venkatesh, Michael Synodis, James H. Pikul, Sue Ann Bidstrup Allen, and Mark G. Allen



batteries") are critical power sources for microelectromechanical system (MEMS)based sensors and actuators. However, the achievable volumetric and gravimetric energy densities of microbatteries are typically insufficient for intermediate-term applications of MEMS-enabled distributed internet-connected devices. Further, in the increasing subset of Internet of Things (IoT) nodes, where actuation is desired, the peak power density of the microbattery must be simultaneously considered. Metal—air approaches to achieving microbatteries are attractive, as the anode and cathode are amenable to miniaturization; however, further improvements in energy density can be obtained by minimizing the electrolyte volume. To investigate these potential improvements, this work studied very lean hydrogel electrolytes based on poly(vinyl alcohol) (PVA). Integration of high potassium hydroxide (KOH) loading into the PVA hydrogel improved electrolyte performance. The addition of



potassium carbonate (K_2CO_3) to the KOH–PVA gel decreased the carbonation consumption rate of KOH in the gel electrolyte by 23.8% compared to PVA-KOH gel alone. To assess gel performance, a microbattery was formed from a zinc (Zn) anode layer, a gel electrolyte layer, and a carbon–platinum (C–Pt) air cathode layer. Volumetric energy densities of approximately 1400 Wh L⁻¹ and areal peak power densities of 139 mW cm⁻² were achieved with a PVA–KOH– K_2CO_3 electrolyte. Further structural optimization, including using multilayer gel electrolytes and thinning the air cathode, resulted in volumetric and gravimetric energy densities of 1576 Wh L⁻¹ and 420 Wh kg⁻¹, respectively. The batteries described in this work are manufactured in an open environment and fabricated using a straightforward layer-by-layer method, enabling the potential for high fabrication throughput in a MEMS-compatible fashion.

KEYWORDS: Zn–air, microbatteries, very lean electrolyte, high energy density, hydrogel, PVA–KOH–K₂CO₃ gel electrolyte

1. INTRODUCTION

The Internet of Things (IoT),¹ comprising wireless transducers, communication relays, and information processing hubs, is becoming widespread; however, the nodes of such systems can often require onboard energy storage sources.¹⁻⁴ In particular, as the IoT matures, nodes are beginning to incorporate actuation into their functionality. Although there has been rapid development in both physical micromanufacturing and information technology that continues to drive such systems toward miniaturization, the lack of reliable energy sources of comparable size becomes a significant limitation.^{4,5} In particular, the energy and power requirements for smallscale IoT actuator nodes may necessitate new approaches to the realization of small-scale power sources within this new design space.

As one example, insect-scale robots, envisioned as a powerful tool for search, rescue, and confined environment exploration, suffer from limited operational speed, constraints on additional payload, and short operation time.⁶ The level of maneuver-

ability required for micro aerial vehicles also dictates the onboard power consumption and can result in mission-limiting flight restrictions, such as limited flight duration and range.⁷ Small-scale, primary electrochemical energy storage devices ("microbatteries") of both high energy and high peak power density are needed to meet the above requirements.⁵ Commercial lithium (Li)–polymer and Li-ion batteries are most commonly used for modern robots, however, as the size scales down, the proportion of the battery containing active material relative to packaging and other battery components decreases rapidly.^{7,8}

Received: November 6, 2022 Accepted: January 12, 2023 Published: January 26, 2023





Metal-air batteries are of particular interest in this new design space because of their high-energy-density compared with lithium (Li)-ion batteries.9 A notable characteristic of metal-air batteries is that their cathode active material is oxygen from ambient air. Since this oxygen is not enclosed within the battery, additional space for energy storage material and/or reduced battery weight is achievable.¹⁰⁻¹² Among metal-air battery anodes, Li, zinc (Zn), magnesium (Mg), and aluminum (Al) have attracted much interest.¹¹ Although Liair has the highest theoretical gravimetric energy density due to the electrochemical activity and low density of Li metal, the achievable practical energy density is typically lower at the small scale due to the overhead of the battery structure, electrolyte, separator, and package required to house Li metal.¹³ Al and Mg not only have relatively high energy densities but also have high self-discharge rate, and discharge products may limit anode utilization.^{10,11} The Zn-air system is particularly promising for microbattery applications due to its large theoretical energy density, safety, relatively low corrosion current, and stable discharge voltage. Further, its openenvironment fabrication and minimal packaging requirements result in favorable microbattery scalability. Therefore, the Znair system has been proposed as a potential substitute even for commercial Li-ion microbatteries.^{10,14,15}

Within the Zn-air system, tremendous effort has been devoted both to the development of cathode catalytic materials as well as the structural details of the Zn anode; however, relatively less attention has been paid to the electrolyte itself. For example, when considering the specific energy or capacity of Zn-air batteries, work on Zn utilization in an excess electrolyte, whether in aqueous or hydrogel form, focuses on the mass of the anode without considering the mass and volume of the electrolyte. This is appropriate when conducting studies on anode performance, whether in terms of specific capacity or energy density; however, care must be taken when extrapolating these results to full battery performance. For example, Mohamad demonstrated that the specific capacity density of a primary Zn-air battery with the gel electrolyte is 657.5 mA h g^{-1} Zn. However, the capacity density of the entire battery drops to 18.58 mA h g^{-1} , if taken with respect to the weight of the entire cell including the electrolyte.¹⁶ Abbasi and co-workers developed a new hydroxide exchange membrane for a Zn-air battery and achieved a maximum specific energy density of 1000 mW h g⁻¹ Zn (Zn anode 1×1 cm² \times 0.1 mm). However, when 40 mL of 7 M KOH electrolyte is included, the energy density drops to 13.6 mW h g^{-1} .¹⁷¹⁷ When considering the overall battery energy density, especially for smaller-scale applications, careful optimization of the quantity of electrolytes will be a key factor in maximizing the energy density of the battery. This work will therefore focus on developing a lean electrolyte for Zn-air batteries to improve their overall energy density and peak power density for miniaturized actuator applications.

Design of a minimum volume/weight electrolyte should take into account the overall chemistry of the Zn–air system as well as detrimental and side reactions that may occur during battery discharge. For Zn–air chemistry in an alkaline electrolyte, multiple-step anodic reactions are¹⁰

$$Zn + 4OH^{-} \rightarrow Zn(OH)_{4}^{2-} + 2e^{-}$$
$$Zn(OH)_{4}^{2-} \rightarrow ZnO + H_{2}O + 2OH^{-}$$

The cathodic reaction is

$$O_2 + 4e^- + 2H_2O \rightarrow 4OH$$

And the overall reaction is

$$2Zn + O_2 \rightarrow 2ZnO$$

According to the above equations, there is theoretically no net consumption of hydroxide ion or water during discharge; thus, the design of a minimum volume electrolyte for a particular desired battery performance is possible. However, multiple studies have shown hydroxide ion consumption during cell discharge.^{10,18-20} For example, relatively slow zincate decomposition at the early stages of discharge could lead to slow regeneration of hydroxide ions.^{19,21-23} Further, since the Zn-air battery uses alkaline electrolyte and has an open cell structure (i.e., exposed to ambient air), the carbon dioxide (CO_2) present in the air can react with the hydroxide ion in the electrolyte and form carbonate ions, thereby depleting hydroxide ions.²⁴⁻²⁷ Thus, in practice, the concentration of the hydroxide ion decreases over time during discharge, which could cause the deterioration of the battery. The problem worsens with a limited volume electrolyte and a long-duration use case and may dominate an electrolyte design. Electrolyte additives have been shown to ameliorate this problem. For example, Schröder et al. have reported that adding potassium carbonate (K₂CO₃) to an aqueous alkaline electrolyte mitigates electrolyte carbonation without lowering the ionic conductivity of the electrolyte.²²

Additives such as K₂CO₃ are used not only in aqueous alkaline electrolytes but also in polymer hydrogel electrolytes. The use of the hydrogel electrolyte can solve the leakage and volatilization issues of liquid electrolytes, simultaneously serving as a seperator and electrolyte solution host, which simplifies the battery structure and has the potential to further reduce the size of the battery.²⁹ For example, the poly(vinyl alcohol) (PVA) hydrogel electrolyte can function as both the separator and KOH carrier, given its ability to provide both good ionic conductivity and mechanical stability.^{29,30} PVA is also recognized as an inexpensive, easily prepared biodegradable polymer and has been widely used in electrochemical devices, such as fuel cells, alkaline batteries, supercapacitors, and metal-air scavengers.³¹⁻³³ Abdulkadir et al. have reported that the addition of K₂CO₃ to PVA gel electrolytes improves the homogeneity and even the conductivity of the polymer composite by softening the polymer backbone.³⁴

Recognizing the importance of the electrolyte volume in high energy and power density microbatteries, we report a lean PVA-KOH-K2CO3 gel electrolyte for the Zn-air battery chemistry that significantly improves both energy and power density due to a minimized electrolyte volume, with the intended application of small-scale IoT actuator nodes. A systematic study of the performance of hydrogel electrolytes of different thicknesses and compositions is undertaken, navigating the tradeoff between the gel electrolyte volume, gel additives, and total output energy and power density of microbatteries containing these hydrogel electrolytes. Noting that in this lean electrolyte system, a potential cause of battery capacity decay could be a shortage of the hydroxide ion due to carbonation and zincate accumulation, and the use of high KOH loading and K₂CO₃ additives was emphasized. These compositions were found to effectively mitigate hydroxide ion depletion; the corresponding lean electrolyte batteries deliver a much higher energy density than typical 6M hydroxide-ion-

www.acsami.org

Table 1. Gel Electrolytes Fabricated in This Study

gel type	precursor	thin	thick	rehydrated with 6M KOH	rehydrated with saturated KOH	rehydrated with saturated $\rm KOH/K_2CO_3$
type 1	KOH/PVA	х			Х	
type 2	KOH/PVA		Х	Х		
type 3	KOH/PVA		Х		Х	
type 4	KOH/K ₂ CO ₃ /PVA		Х			Х



Figure 1. Gel preparation. (a) Precursor solutions of KOH gel (clear) and K_2CO_3 gel (cloudy). (b) KOH gel films after laser patterning. The gel in the field has been removed leaving behind gel film discs. (c) KOH gel sheet formed in Petri dish. (d) KOH and K_2CO_3 sheet discs. Note that the carbonate-containing gels are white in color, while the KOH-only gels are transparent.



Figure 2. Top-down view of the battery assembly process. (a), (b) Zn anode is placed on a Plexiglas holder, and a KOH gel and a K_2CO_3 gel are placed on top of the Zn anode, respectively. (c) Pt-carbon cathode is placed on top of the KOH gel/Zn anode multilayer. (d) Fully assembled battery for the test with an upper Plexiglas holder placed on top of the cathode. The entire structure is tightened by a pair of screws. (e) Schematic view of battery components.

loaded hydrogels previously adopted for high ionic conductivity (and therefore high peak power density).³

2. EXPERIMENTAL SECTION

2.1. Fabrication. 2.1.1. Alkaline Gel Electrolyte Fabrication. Electrolyte gels based on poly(vinyl alcohol) (PVA) with various additives and prepared using various techniques were explored in this study. Electrolyte gels were differentiated by thickness (thinner spincast films vs thicker solution-cast sheets) and additive content (KOH-only vs KOH/K₂CO₃). Further, some gels were rehydrated in 6M KOH solution, some in saturated KOH solution, and some in saturated KOH solution with added K₂CO₃. These differentiations led to the study of four distinct gels as outlined in Table 1: (i) KOH films rehydrated in saturated KOH; (iii) KOH sheets rehydrated in 6M KOH; (iii) KOH sheets rehydrated in a attrated KOH; and (iv) KOH/K₂CO₃ sheets rehydrated in a rehydration solution prepared by adding K₂CO₃ to a saturated KOH solution in the mass ratio of 1:5.27. The fabrication of each of these gels will be described below.

Two types of gel electrolyte precursors were explored. The KOH/ PVA gel electrolyte precursor was made by first dissolving 1.5 g of PVA (MW 88,000–98,000, hydrolyzed 90%, Alfa Aesar) in 10 mL of deionized (DI) water. The mixture was heated to 85 °C and vigorously stirred at 700 rpm for 3 h. After the PVA solution cooled to room temperature, an alkaline solution produced by dissolving 1.5 g of KOH (85%, Sigma-Aldrich) in 5 mL of DI water was added dropwise to the PVA solution.³⁵ The solution was stirred continuously for approximately 1 h at room temperature to form the uniform KOH gel precursor. The KOH/K₂CO₃/PVA gel electrolyte precursor was prepared in the same fashion, except the alkaline solution consisted of 1.5 g of KOH and 0.64 g of K₂CO₃ in 10 mL of water, which was added dropwise to the PVA solution following the same procedure as that of the KOH/PVA gel precursor. Gel electrolytes were formed from the precursor solution using two methods: spin-casting (type 1) and solution-casting (types 2–4). To form spin-cast gel films, a soda lime glass substrate with a size of 3 in. \times 2 in. and a 0.039–0.047 in. thickness was first rinsed using isopropyl alcohol (IPA) and dried with a nitrogen gun; this rinsing was also found to facilitate subsequent removal of the gel sheet from the glass substrate after drying. A layer of the KOH/PVA gel precursor was spin-cast at 100 rpm for 30 s and dried in a desiccator for approximately 1 h to form a film. Gel films of thickness approximately 10–30 μ m as measured using optical microscopy were achieved by spin-coating. After gel film formation, the gel films were patterned into discs or toroidal rings of desired sizes using a 193 nm excimer laser (IPG IX-255). The gel discs were subsequently immersed in saturated KOH (type 1) and rehydrated for at least 2 days.

To form solution-cast gel sheets (types 2–4), a glass Petri dish was cleaned using DI water followed by an IPA rinse and nitrogen drying step. Measured quantities by weight of the appropriate gel precursor for a desired final gel thickness were poured into the dish. The dish containing the gel was then dried in a desiccator for 4–10 h depending on the thickness of the gel to let the water slowly evaporate and form a gel sheet. Typical gel sheet thicknesses ranged from 50 μ m to 1 mm. After gel sheet formation, rehydration was carried out in either 6M KOH (type 2), saturated KOH (type 3), or saturated KOH/K₂CO₃ (type 4, where the KOH/K₂CO₃ gel precursor was used). The rehydrated sheets were then cut into discs by a hollow steel punch with a diameter of 0.5 in. Figure 1 shows the various precursors and gel electrolytes at different stages of fabrication.

2.1.2. Microbattery Fabrication. Zinc foils (250 μ m in thickness, 99.99% pure, Sigma-Aldrich) were laser micromachined into specific shapes using a 532 nm machining laser (IPG IX280-DXF machining system). Commercial platinum (Pt)-loaded carbon gas diffusion electrodes (4 mg cm⁻² Pt, fuel cells, etc.) were used as the air cathode



Figure 3. (a) Mass-normalized hydroxide ion concentration of gels rehydrated by 6M KOH (type 2) and saturated KOH (type 3) solutions. (b) Comparison of total extracted energy from batteries formed with type 2 and type 3 gels of various masses. (c) Type 3 gel mass-volume relationship showing constant gel density. (d) Total amount of OH^- in type 3 and type 4 gels as a function of gel mass.

material. A 193 nm excimer laser (IPG IX-255) was used to pattern the cathode into a 1 cm diameter circular shape. Full batteries are assembled by alternating layers of the cathode, gel electrolyte, and anode. Figure 2a,b shows a KOH gel and a K_2CO_3 gel, respectively, on top of a Zn anode. Figure 2c shows a Pt–carbon cathode on top of the KOH gel/Zn anode multilayer. A 120 lines-per-in. Ni mesh (Precision Eforming) was placed above the cathode for cathode electrical connection; the mesh nature of this electrode preserved air transport through the electrode to the cathode. The entire battery assembly was then clamped between two Plexiglas holders and tightened by a pair of screws to ensure good interlayer mechanical contact. The Plexiglas holder facing the cathode has air diffusion holes formed by CO_2 laser machining (PLS 4.75, Universal Laser Systems), as shown in Figure 2d. Figure 2e shows a schematic of the battery's active components.

2.2. Characterization. 2.2.1. Quantitative Chemical Analysis. The hydroxide ion and carbonate ion concentrations in the gel electrolyte were measured by two-step volumetric titration under ambient conditions.²⁰ The titrand was prepared by immersing the gel electrolyte into 200 mL of DI water for over 12 h (it was found that longer immersion times did not alter subsequent titration results). The titrand was titrated against 0.01 M HCl (Sigma-Aldrich) using phenolphthalein (0.5 wt %, Sigma-Aldrich) and bromocresol green (0.1% w/v, Fisher) indicators.

Phenolphthalein was first added to the titrand, the color of which changed from pink to light pink at pH = 8.2, when all of the hydroxide ions and carbonate ions were turned into water and bicarbonate ions, respectively. The volume of titrant consumed in step 1 is V_1 . The bromocresol green was then added to the titrand, the color of which changed from blue to green at pH = 4.2, representing the end of the reaction of bicarbonate ions and hydrogen ions. The total volume of the consumed titrant in steps 1 and 2 was recorded as V_2 . Then, the amount of hydroxide ions is given by

$$_{I^-} = (2V_1 - V_2)^* M_{\text{titrant}}$$

n_{OE}

The amount of carbonate ions is

$$n_{\rm CO_2^{2-}} = (V_2 - V_1)^* M_{\rm titrant}$$

where $M_{\rm titrant}$ represents the molarity of the titrant.

2.2.2. Electrochemical Characterization. 2.2.2.1. I-V Scan. Galvanodynamic potential measurements were performed using a BioLogic BCS-805 Ultraprecision battery cycler to characterize the maximum power capability of the battery. An I-V curve was measured by scanning the assembled battery from 0 to 100 mA with a scan rate of 10 mA s⁻¹. The lower limit voltage was set to be 0 V.

2.2.2.2. Impedance Test. Electrochemical impedance spectroscopy (EIS) measurement was performed using a Gamry Reference 600 in the frequency range of 0.5 Hz to 10 kHz with a 10 mV perturbation amplitude under no-bias conditions.

2.2.2.3. Multistep Discharge with Interval. The energy output of the batteries was measured using a sequential constant current discharge using the BioLogic BCS-805, during which the discharge current was progressively lowered from 10 to 0.25 mA through a multistep discharge (10-7.5-5-2.5-1-0.75-0.5-0.25 mA). At the start, the current was set to 10 mA, and cell discharge proceeded until the cell voltage dropped to zero. The discharge current was then reduced to zero, and the cell was rested for 15 min under ambient conditions to allow any redistribution of hydroxide ions to occur. The cell was then discharge dat the next lower current in the sequence, and the cycle was repeated. Once the discharge voltage reached zero under 0.25 mA discharge, further testing was terminated. The energy removed from the cell during each discharge sequence was then added to determine the total energy content of the cell.

2.2.2.4. CO_2 -Free Test Environment. Our previous work has demonstrated that carbonation is not the sole mechanism of hydroxide ion consumption.²⁰ Another cause of the hydroxide consumption is the formation and slow decomposition of the intermediate product zincate ion.^{19–22} To isolate the carbonation effect from the zincate consumption, a CO_2 -free environment was built to test the battery for reference.

To achieve this test environment, compressed air was bubbled through a beaker containing saturated KOH solution to absorb the CO_2 in the air. The resultant gas was then conducted into a closed box with an exhaust port. After approximately 15 min, the majority of



Figure 4. (a) Zincate ion accumulation in type 3 (KOH) and type 4 (KOH $-K_2CO_3$) gels under 10 and 1 mA discharge conditions. (b) Carbonation rate of type 3 and type 4 gels. (c) Ionic conductivity at open-circuit potential versus time for type 3 and type 4 gels.

the CO_2 content was removed from the box ambient. A CO_2 -humidity meter (Extech SD800) was enclosed in the box to monitor the environment. The CO_2 in ambient air is approximately 400 ppm. In the box, the CO_2 concentration was reduced to approximately 20 ppm.

It was found that the high-concentration KOH filtering solution also reduced the humidity of the CO_2 -free gas. When the relative humidity dropped below 30% RH, the gel mass decreased over time due to the loss of water content to the environment. The lower the water content of the gel, the lower the ionic conductivity, which could lead to battery failure.³⁶ Therefore, a humidifier was placed within the box to maintain the humidity at 40–55% RH.

3. RESULTS AND DISCUSSION

3.1. KOH Loading of Gels. The total amount of hydroxide ions in various gels, determined by two-step titration, was then normalized by the mass of the gel to yield a normalized hydroxide ion loading of each gel. Figure 3a shows the normalized hydroxide ion loading of KOH gel discs rehydrated in 6M KOH (type 2) and in saturated KOH (type 3) solutions. Average values are taken from 4 of type 2 gels and 4 of type 3 gels with masses ranging from 40 to 80 mg. On a normalized basis, type 3 gels contain 44% more hydroxide ions than type 2 gels. Figure 3b shows the total energy extracted from batteries fabricated from type 2 and type 3 gels. Type 3 gel batteries can deliver significantly more energy than type 2 gels at all gel masses. As an example, a battery made from a 54 mg type 3 gel, with normalized hydroxide concentration of 6.5×10^{-6} mol mg⁻¹ KOH, was able to deliver 40 mW h, approximately eight times as much energy as a battery made from a 54 mg type 2 gel, with a normalized hydroxide ion concentration of 4.5 \times 10^{-6} mol g⁻¹ KOH, which was able to deliver 5 mW h.

To explore the relationship between the mass and volume of these gels, type 3 gel masses (obtained by weighing) and volumes (obtained by optical microscopy) were determined prior to discharge tests. As shown in Figure 3c, the type 3 gel mass—volume relationship was linear with an average density of approximately 1.47 g cm⁻³. Figure 3d shows the relationship between the total amount of hydroxide ions and the mass of type 3 gels and type 4 gels (i.e., gels containing K₂CO₃ additive). The linear hydroxide ion—gel mass relationship for both gels not only supports the use of the mass-normalized loading concept for gel characterization but also shows that the mass-normalized hydroxide ion concentration for type 3 and type 4 gels is similar at 7×10^{-6} mol mg⁻¹, implying minimal effects of the carbonate additives on normalized hydroxide ion loading of gels.

3.2. Effect of K_2CO_3 Additive on Zincate Decomposition Rate and Carbonation Rate. As discussed previously, in principle, the battery chemistry under discussion should yield no net hydroxide ion consumption during battery discharge. However, in practice, hydroxide ion consumption can occur from at least two sources: zincate accumulation and carbonation.

During battery discharge, the intermediate species zincate ion is produced. Zincate ion generation consumes the hydroxide ion, which is subsequently regenerated when the zincate ion decomposes into zinc oxide. Under higher discharge rate conditions, the zincate ion may accumulate; in such cases, the hydroxide ion concentration will be lowered.²⁰ To investigate this effect, zincate accumulation under 1 and 10 mA discharge conditions is plotted in Figure 4a for batteries fabricated from type 3 (saturated KOH) and type 4 (KOH- K_2CO_3) gel electrolytes. The detailed procedures for measuring carbonation rates and zincate accumulation rates using titration are described in ref 20. For 10 mA discharge experiments, the average type 3 and type 4 gel masses were 125.1 and 126.3 mg, respectively; while for 1 mA discharge experiments, the average type 3 and type 4 gel masses were



Figure 5. (a) Cell potential vs current density, and current density vs areal power density curves for a battery with type 1 KOH gel electrolyte. (b) Peak power densities vs mass of the gel for batteries with type 4 K_2CO_3 gel electrolyte. (c) Total output energy comparison of batteries comparing type 4 K_2CO_3 gels discharged in ambient air with type 1 and type 3 saturated KOH gels discharged in ambient air and the CO₂-free box. (d) Device-level volumetric energy density of type 4 K_2CO_3 gel batteries discharged in ambient air as a function of gel mass.

35.4 and 41 mg, respectively. The zincate accumulation process tends to reach a steady state, which agrees with the results reported previously.³⁷Figure 4a shows no significant difference in zincate accumulation between the two types of electrolytes under 1 mA discharge conditions. Under 10 mA discharge conditions, the zincate accumulation process in type 4 gels reaches a steady state earlier than in type 3 gels, suggesting that the addition of K₂CO₃ may delay zincate accumulation.

Hydroxide ions can also be consumed by the carbonation process. Since the electrolyte is in contact with ambient air at the electrolyte-cathode interface, carbon dioxide from ambient air can react with the hydroxide ion in the electrolyte causing hydroxide ion loss. To assess this effect, the two-step titration introduced in Section 2.2 is used to measure the remaining hydroxide ions in type 3 and type 4 gel electrolytes at 0, 100, and 200 min. Three gels for each type of gel electrolyte were stored under ambient conditions for 0, 100, and 200 min before the titration. The carbonation rate was calculated by normalizing the linear decreasing rate of the hydroxide ions over time by the exposed area (footprint of the gel discs). These carbonation measurements are repeated three times for each type of gel electrolyte.

The average value with a standard error bar of three carbonation rate measurements of each type of gel is shown in Figure 4b. The carbonation rate of type 4 K_2CO_3 gel electrolyte is 23.8% lower than that of type 3 KOH gel electrolyte. The modeling of the carbonation process shows

that the carbonation rate is governed by both carbon dioxide diffusion in the electrolyte and the concentration of hydroxide and carbonate in the electrolyte.²⁰ In type 4 K₂CO₃ gel electrolyte, the added carbonate content in the electrolyte reduces the driving force of the carbonation reaction. For example, carbon dioxide could have smaller diffusivity in the liquid content of the PVA–KOH–K₂CO₃ hydrogel, thus reducing the carbonation rate.²⁷ This potential mechanism is supported by findings that the addition of K₂CO₃ to KOH solutions increases the solution viscosity.³⁸

Since the ionic conductivity of the gel electrolyte is also related to the hydroxide ion concentration, the gel ionic conductivity as a function of time was assessed. Tests were performed under open-circuit conditions to minimize the effect of zincate ion accumulation and potentially correlate ionic conductivity loss with carbonation.²⁴Figure 4c shows the ionic conductivity measurements of the electrolytes under opencircuit potential. All EIS measurements were performed under ambient environment, and EIS measurements were repeated three times for each type of electrolyte. The high-frequency intercept on the real impedance axis was ascribed to ionic resistivity of the electrolyte. The average masses were 43.2 and 44.2 mg for type 3 (KOH) and type 4 (K_2CO_3) gels, respectively. The initial ionic conductivity of type 4 gel electrolyte was approximately 10% higher than type 3 gel. This observation agrees with previous reports that the introduction of K₂CO₃ salt increases the amorphous phase of the polymer, improving its ionic conductivity.³⁴ Ionic conductivity gradually



Figure 6. (a) Configuration of the optimized battery of this work having the highest energy density under ambient conditions. (b) Multistep discharge curve (from 10 to 0.25 mA) of this optimized battery.^{32,38–42}

declined over time for both gels. Due to the superior carbonation resistance of type 4 gel, the ionic conductivity of type 4 gel decreased at a slower rate $(3.7 \text{ mS cm}^{-1} \text{ over } 20,000 \text{ s})$ than that of type 3 gel (5.1 mS cm⁻¹ over 20,000 s).

3.3. Electrochemical Performance. Figure 5a shows the cell potential of a battery with 12 μ m saturated KOH gel electrolyte (type 1) versus discharge current density, which suggests a peak areal power density of 117.5 mW cm⁻² at a current density of 115.3 mA cm⁻². The initial small overpotential indicates that the reaction is kinetics limited at this region. In the middle region, the relation between voltage and current density is linear, suggesting that the reaction is ohmic-limited. For the region where the current density is over 120 mA cm⁻², there is a sudden drop of voltage due to oxygen diffusion limitation, in which the transport of the oxygen cannot sustain the high current.³⁹Figure 5b shows the peak power density of batteries with type 4 K₂CO₃ gels of various masses. As the gel thickness (and therefore gel mass) increases, the peak power density decreases, potentially due to the higher total electrolyte resistance of the thicker gels.

Figure 5c shows the maximum energy output from batteries built with gels varied by mass and composition through the multistep discharge. The energy output per unit gel mass from type 4 K₂CO₃ gel is higher than that of type 3 KOH gel in ambient air and is closer to that of type 3 gel tested in the CO₂-free box. The performance is consistent with the observation that type 4 gel with carbonate additive has a lower hydroxide ion consumption rate due to carbonation compared to the KOH-only type 3 gels; when carbonation is suppressed due to the removal of CO₂ from the ambient air, the performance of the two gels converges.

For thin gels with a mass below 30 mg, it is observed that the batteries tested in ambient air delivered negligible energy. This could be due to the very limited amount of hydroxide ions stored in the thin gels, which might decrease to the level that cannot sustain any discharge during the resting time between the discharge steps. The type 4 K_2CO_3 gel has a similar threshold (20–30 mg) to the KOH gel in the air.

The maximum energy output from batteries tested in the CO_2 -free box began to plateau when gel masses exceeded approximately 80 mg. The transition mass for batteries discharged in air lagged behind that of the batteries discharged in the CO_2 -free box, which is consistent with continued carbonation during the longer discharge lifetimes of higher energy cells. The plateau-shaped energy curve of the batteries also suggests a transition from a gel-limiting condition to a Zn-

limiting condition. When the gel is thin, there is excess Zn, and the battery performance is limited by the gel. However, as the gel thickness (and therefore mass) increases, and the Zn utilization exceeds approximately 85%, the maximum energy of the battery tends to be limited by the anode. In this latter region, additional gel does not further improve the maximum energy. The similar plateau energy of batteries in the CO_2 -free box and batteries in the air supports this hypothesis because the amount of Zn used is kept constant for all discharge tests (it should be noted that although the value of the plateau energy is similar, for the ambient air case, additional gel mass may be required to achieve the energy plateau to compensate for the carbonation-based consumption of hydroxide ions).

Therefore, a potential optimization path toward the highest energy density for these batteries may be to select a gel mass such that the maximum possible energy output from the gel equates to the upper limit of what the zinc anode can practically provide. Figure 5d shows the device-level volumetric energy densities of batteries formed from K_2CO_3 gels discharged under ambient conditions. In this calculation, nominal values of Zn anode and cathode volumes were used for each battery. The volumetric energy density reached approximately 1400 Wh L⁻¹ at approximately 80 mg gel mass.

Based on these data, further optimization was carried out to maximize both the volumetric and gravimetric energy densities of these Zn-air batteries operating in ambient air. In addition to optimization of the gel electrolyte, the optimization of the cathode and the construction of the battery itself were further explored. The volumetric energy density of the batteries was further improved by reducing the cathode thickness to 90 μ m and by mechanical grinding of the cathode gas diffusion layer. To investigate the effect of the interfacial area between the gel electrolyte and the Zn anode surface on the total output energy, batteries with two gels sandwiching the Zn anode with a central hole to facilitate ionic diffusion between the gels were assembled and tested as shown in Figure 6a. The two-sided gel/anode construction in some cases delivered a slightly higher total energy compared to the single gel structure, although this improvement was not consistently observed. Nevertheless, the highest energy densities of 1576 Wh L^{-1} and 420 Wh kg^{-1} were reached by a two-sided gel/anode configuration with type 4 PVA-KOH-K₂CO₃ gel electrolytes. Figure 6b shows the multistep discharge curve of this battery. The blue curve and black curve present the voltage recorded at resting time and the discharge voltage, the red line shows the discharge current of corresponding steps, which is drawn

www.acsami.org



Figure 7. Device level volumetric energy density and peak power density (based on the total anode, cathode, and electrolyte volume) of the optimized battery of this work compared with others in the literature. $^{35,41-45}$

against the secondary y-axis. The higher energy density of this cell is potentially due to the higher Zn-gel interfacial area reducing the surface concentration of the ZnO reaction product, therefore delaying the passivation of the Zn anode.^{11,40} The observation of the passivation layers formed on both the top and bottom Zn-gel interface of discharged two-sided gel/anode batteries versus the single passivation layer formed on the top Zn-gel interface of discharged single gel batteries supports this hypothesis.

A comparison plot of various Zn-air batteries in the literature, together with the performance of the optimized battery of this work, is given in Figure 7. It should be noted that it is challenging to make direct comparisons of this type because various batteries have different structures, discharge profiles, and packaging approaches. When constructing this comparison, values of energy density and peak power density were obtained by dividing the total reported energy or peak power produced by the battery by the sum of the volumes of the anodes, cathodes, and electrolytes. The gel-optimized batteries described here compare favorably with those in the literature, illustrating the utility of optimizing lean electrolyte gels for high energy and peak power density Zn-air batteries.

We also compared the performance of the battery of this work with a commercial Zn-air battery (type 312, Amazon Basics) that has been widely used in hearing aid applications with the detailed data displayed in Table 2. The output capacity and energy of the optimized battery developed in this

Table 2. Summary of Cell Performance Data in Ambient Air^{a}

parameter	this we	ork	type 312	
footprint area (cm ²)	0.784		0.490	
battery volume (cm ³)	0.0599		0.160	
battery mass (g)	0.225		0.540	
discharge rate (h ⁻¹)	0.0596C	0.125C	0.0436C	0.125C
total capacity (mA h)	80.0	29.8	160	0.941
total energy (mW h)	94.4	34.7	143	0.418
gravimetric energy density (Wh kg ⁻¹)	420	154	265	0.774
volumetric energy density (Wh L^{-1})	1576	579.3	893.8	2.613

^aData for this work taken from measurements of an optimized cell; data for the commercial 312 battery taken from measurements in lab. Batteries of this work and type 312 tested by the multistep discharge with an average discharge rate of 0.0596C and 0.0436C calculated based on the total lifetime. The batteries tested under a single high discharge rate at 0.125C. work are approximately 32 times and 83 times that of the commercial 312 Zn-air battery at 0.125C discharge rate, which shows the improved performance at a high discharge rate.

4. CONCLUSIONS

Utilization of lean electrolytes based on alkaline hydrogels with carbonation-suppressing additives is an attractive approach to realize high-energy-density air battery power sources. PVAbased KOH gel electrolytes of thicknesses ranging from 10 μ m to 1 mm were fabricated by spin-coating and solution-casting methods. The introduction of the additive K₂CO₃ reduced the carbonation rate of these electrolytes by 23.8% and mitigated the decreases of the resultant ionic conductivity. To realize microbatteries, such hydrogels can be formed in a single layer (on top of the anode) or multilayer (surrounding the anode) configuration; the layered structure of these batteries facilitates a straightforward fabrication and assembly process. Illustrating the performance of the electrolyte, a primary Zn-air microbattery based on a multilayer gel configuration achieved volumetric and gravimetric energy densities of 1576 Wh L⁻¹and 420 Wh kg⁻¹ in ambient air. The power performance of these microbatteries was also investigated with a maximum device level peak power density of 1207 $\rm W~L^{-1}$ and areal peak power density of 139 mW cm⁻² achieved, which shows the potential to supply the burst discharge rate (short-duration, high-current discharge) needed for actuators under conditions, such as the lifting of micro air vehicles.³⁵ Finally, the output capacity under a high discharge rate of 0.125C was found to be more than 30 times that of the commercial coin cell. All of these enhanced performance factors were enabled by careful design of a very lean electrolyte for these energy systems.

AUTHOR INFORMATION

Corresponding Author

Jingwen Zhang – Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; orcid.org/0000-0002-9354-3308; Email: zjwen@seas.upenn.edu

Authors

- Yanghang Huang Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States
- Qi Yang Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Vishal Venkatesh – Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Michael Synodis – Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

James H. Pikul – Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States; orcid.org/0000-0002-7018-2925

Sue Ann Bidstrup Allen – Department of Chemical and Biomolecular Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Mark G. Allen – Department of Electrical and Systems Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104, United States

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.2c19970

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was funded by the Defense Advanced Projects Research Agency contract HR0011-19-C-0039. This work was also carried out in part at the Singh Center for Nanotechnology, which is supported by the NSF National Nanotechnology Coordinated Infrastructure Program under grant NNCI-2025608. The authors would also like to thank Dr. Min Wang and Dr. Xiujun Yue for their valuable technical discussion.

REFERENCES

(1) Raj, A.; Steingart, D. Review—Power Sources for the Internet of Things. J. Electrochem. Soc. 2018, 165, B3130–B3136.

(2) Pikul, J. H.; Ning, H. Powering the Internet of Things. Joule 2018, 1036-1038.

(3) Zhu, Z.; Kan, R.; Hu, S.; He, L.; Hong, X.; Tang, H.; Luo, W. Recent Advances in High-Performance Microbatteries: Construction, Application, and Perspective. *Small* **2020**, *16*, No. e2003251.

(4) Wang, Y.; Liu, B.; Li, Q.; Cartmell, S.; Ferrara, S.; Deng, Z. D.; Xiao, J. Lithium and Lithium Ion Batteries for Applications in Microelectronic Devices: A Review. *J. Power Sources* **2015**, *286*, 330– 345.

(5) Bandari, V. K.; Schmidt, O. G. System-Engineered Miniaturized Robots: From Structure to Intelligence. *Adv. Intell. Syst.* 2021, *3*, No. 2000284.

(6) Goldberg, B.; Zufferey, R.; Doshi, N.; Helbling, E. F.; Whittredge, G.; Kovac, M.; Wood, R. J. Power and Control Autonomy for High-Speed Locomotion with an Insect-Scale Legged Robot. *IEEE Robot. Autom. Lett.* **2018**, *3*, 987–993.

(7) Farrell Helbling, E.; Wood, R. J. A Review of Propulsion, Power, and Control Architectures for Insect-Scale Flapping-Wing Vehicles. *Appl. Mech. Rev.* **2018**, *70*, No. 021003.

(8) GEB Lithium Ion Polymer Battery Series, 2022. http://www.gebattery.com.cn/product/product.php?class2=115.

(9) Chawla, N. Recent Advances in Air-Battery Chemistries. *Mater. Today Chem.* **2019**, *12*, 324–331.

(10) Lee, J. S.; Kim, S. T.; Cao, R.; Choi, N. S.; Liu, M.; Lee, K. T.; Cho, J. Metal-Air Batteries with High Energy Density: Li-Air versus Zn-Air. *Adv. Energy Mater.* **2011**, *1*, 34–50.

(11) Rahman, M. A.; Wang, X.; Wen, C. High Energy Density Metal-Air Batteries: A Review. J. Electrochem. Soc. **2013**, 160, A1759– A1771. (12) Linden, D.Handbook of Batteries. In *Fuel and Energy Abstracts;* Elsevier Science, 1995; Vol. 33.

(13) Girishkumar, G.; McCloskey, B.; Luntz, A. C.; Swanson, S.; Wilcke, W. Lithium-Air Battery: Promise and Challenges. J. Phys. Chem. Lett. 2010, 1, 2193–2203.

(14) Caramia, V.; Bozzini, B. Materials Science Aspects of Zinc-Air Batteries: A Review. *Mater. Renewable Sustainable Energy* **2014**, *3*, No. 28.

(15) Zhang, J.; Zhou, Q.; Tang, Y.; Zhang, L.; Li, Y. Zinc-Air Batteries: Are They Ready for Prime Time? *Chem. Sci.* **2019**, *10*, 8924–8929.

(16) Mohamad, A. A. Zn/Gelled 6 M KOH/O2 Zinc-Air Battery. J. Power Sources 2006, 159, 752–757.

(17) Abbasi, A.; Hosseini, S.; Somwangthanaroj, A.; Mohamad, A. A.; Kheawhom, S. Poly (2,6-Dimethyl-1,4-Phenylene Oxide)-Based Hydroxide Exchange Separator Membranes for Zinc–Air Battery. *Int. J. Mol. Sci.* **2019**, *20*, No. 3678.

(18) Guo, Y.; Yuan, P.; Zhang, J.; Xia, H.; Cheng, F.; Zhou, M.; Li, J.; Qiao, Y.; Mu, S.; Xu, Q. Co2P–CoN Double Active Centers Confined in N-Doped Carbon Nanotube: Heterostructural Engineering for Trifunctional Catalysis toward HER, ORR, OER, and Zn–Air Batteries Driven Water Splitting. *Adv. Funct. Mater.* **2018**, *28*, No. 1805641.

(19) Stamm, J.; Varzi, A.; Latz, A.; Horstmann, B. Modeling Nucleation and Growth of Zinc Oxide during Discharge of Primary Zinc-Air Batteries. *J. Power Sources* **2017**, *360*, 136–149.

(20) Huang, Y.Mechanistic Study of Hydroxide Ion Consumption in Ultralean PVA Hydrogel Electrolytes for High Energy Ultracompact Zinc-Air Batteries, (in Preparation).

(21) Zhu, A. L.; Duch, D.; Roberts, G. A.; Li, S. X. X.; Wang, H.; Duch, K.; Bae, E.; Jung, K. S.; Wilkinson, D.; Kulinich, S. A. Increasing the Electrolyte Capacity of Alkaline Zn-Air Fuel Cells by Scavenging Zincate with Ca(OH)2. *ChemElectroChem* **2015**, *2*, 134– 142.

(22) Debiemme-Chouvy, C.; Vedel, J. Supersaturated Zincate Solutions: A Study of the Decomposition Kinetics. J. Electrochem. Soc. 1991, 138, No. 2538.

(23) Arise, I.; Kawai, S.; Fukunaka, Y.; McLarnon, F. R. Numerical Calculation of Ionic Mass-Transfer Rates Accompanying Anodic Zinc Dissolution in Alkaline Solution. *J. Electrochem. Soc.* **2010**, *157*, No. A171.

(24) Li, G.; Wang, Y.; Pan, J.; Han, J.; Liu, Q.; Li, X.; Li, P.; Chen, C.; Xiao, L.; Lu, J.; Zhuang, L. Carbonation Effects on the Performance of Alkaline Polymer Electrolyte Fuel Cells. *Int. J. Hydrogen Energy* **2015**, *40*, 6655–6660.

(25) Schröder, D.; Krewer, U. Model Based Quantification of Air-Composition Impact on Secondary Zinc Air Batteries. *Electrochim. Acta* **2014**, *117*, 541–553.

(26) Zhong, Y.; Liu, B.; Zhao, Z.; Shen, Y.; Liu, X.; Zhong, C. Influencing Factors of Performance Degradation of Zinc-Air Batteries Exposed to Air. *Energies* **2021**, *14*, No. 2607.

(27) Zhao, S.; Liu, T.; Wang, J.; Temitope Bello, I.; Zuo, Y.; Wei, M.; Wang, K.; Lau, K. K. S.; Ni, M. Anti-CO2 Strategies for Extending Zinc-Air Batteries' Lifetime: A Review. *Chem. Eng. J.* **2022**, No. 138207.

(28) Schröder, D.; Sinai Borker, N. N.; König, M.; Krewer, U. Performance of Zinc Air Batteries with Added K2CO3 in the Alkaline Electrolyte. *J. Appl. Electrochem.* **2015**, *45*, 427–437.

(29) Wei, Y.; Shi, Y.; Chen, Y.; Xiao, C.; Ding, S. Development of Solid Electrolytes in Zn-Air and Al-Air Batteries: From Material Selection to Performance Improvement Strategies. *J. Mater. Chem. A* **2021**, *9*, 4415–4453.

(30) Chen, P.; Zhang, K.; Tang, D.; Liu, W.; Meng, F.; Huang, Q.; Liu, J. Recent Progress in Electrolytes for Zn-Air Batteries. *Front. Chem.* **2020**, *8*, No. 372.

(31) Santos, F.; Tafur, J. P.; Abad, J.; Fernández Romero, A. J. Structural Modifications and Ionic Transport of PVA-KOH Hydrogels Applied in Zn/Air Batteries. *J. Electroanal. Chem.* **2019**, *850*, No. 113380. Patent US17/428,9962022. (33) Wang, M.; Gao, Y.; Pikul, J. H. Computer-Free Autonomous Navigation and Power Generation Using Electro-Chemotaxis. *Adv. Intell. Syst.* **2021**, No. 2000255.

(34) Abdulkadir, B. A.; Dennis, J. O.; Fadhlullah Bin Abd; Shukur, M.; Elsayed Nasef, M. M.; Usman, F. Preparation and Characterization of Gel Polymer Electrolyte Based on PVA-K2CO3. *Polym.*-*Plast. Technol. Mater.* **2020**, *59*, 1679–1697.

(35) Synodis, M.; Pikul, J.; Ann Bidstrup Allen, S.; Allen, M. G. Vertically Integrated High Voltage Zn-Air Batteries Enabled by Stacked Multilayer Electrodeposition. *J. Power Sources* **2020**, 449, No. 227566.

(36) Yang, C. C. Chemical Composition and XRD Analyses for Alkaline Composite PVA Polymer Electrolyte. *Mater. Lett.* **2004**, *58*, 33–38.

(37) Horn, Q. C.; Shao-Horn, Y. Morphology and Spatial Distribution of ZnO Formed in Discharged Alkaline Zn/MnO[Sub 2] AA Cells. J. Electrochem. Soc. 2003, 150, No. A652.

(38) Hitchcock, L. B.; Mcilhenny, J. S. Viscosity and Density of Pure Alkaline Solutions and Their Mixtures. *Ind. Eng. Chem.* **1935**, *27*, 461–466.

(39) Bazant, M.Electrochemical Energy Systems; de Gruyter, 2014.

(40) Wu, T. H.; Zhang, Y.; Althouse, Z. D.; Liu, N. Nanoscale Design of Zinc Anodes for High-Energy Aqueous Rechargeable Batteries. *Mater. Today Nano* **2019**, *6*, No. 100032.

(41) Perez-Antolin, D.; Schuhmann, W.; Palma, J.; Ventosa, E. Semi-Flowable Zn Semi-Solid Electrodes as Renewable Energy Carrier for Refillable Zn–Air Batteries. *J Power Sources* **2022**, *536*, No. 231480. (42) Zhang, H.; Qu, Z.; Tang, H.; Wang, X.; Koehler, R.; Yu, M.; Gerhard, C.; Yin, Y.; Zhu, M.; Zhang, K.; Schmidt, O. G. On-Chip Integration of a Covalent Organic Framework-Based Catalyst into a Miniaturized Zn-Air Battery with High Energy Density. *ACS Energy*

Lett. **2021**, *6*, 2491–2498. (43) Saputra, H.; Othman, R.; Sutjipto, A. G. E.; Muhida, R. MCM-41 as a New Separator Material for Electrochemical Cell: Application

in Zinc-Air System. J. Membr. Sci. 2011, 367, 152–157. (44) Lin, C.; Shinde, S. S.; Li, X.; Kim, D. H.; Li, N.; Sun, Y.; Song, X.; Zhang, H.; Lee, C. H.; Lee, S. U.; Lee, J. H. Solid-State Rechargeable Zinc–Air Battery with Long Shelf Life Based on Nanoengineered Polymer Electrolyte. ChemSusChem 2018, 11, 3215– 3224.

(45) Liu, Q.; Wang, Y.; Dai, L.; Yao, J. Scalable Fabrication of Nanoporous Carbon Fiber Films as Bifunctional Catalytic Electrodes for Flexible Zn-Air Batteries. *Adv. Mater.* **2016**, *28*, 3000–3006.

Recommended by ACS

Intrinsically Stretchable Microbattery with Ultrahigh Deformability for Self-Powering Wearable Electronics

Chong Bai, Desheng Kong, et al. OCTOBER 26, 2022 ACS MATERIALS LETTERS

www.acsami.org

READ 🗹

All-In-One Energy Harvesting/Storage Integrated Systems Based on Eggshell Membranes

Giovanni da S. Oliveira, Helinando P. de Oliveira, *et al.* AUGUST 24, 2022 ACS APPLIED ELECTRONIC MATERIALS

READ 🗹

RFAD

Contact-Based Passive Thermal Switch with a High Rectification Ratio

Sampath Kommandur and Ravi Anant Kishore DECEMBER 09, 2022

ACS ENGINEERING AU

Nanostructuring Electrode Surfaces and Hydrogels for Enhanced Thermocapacitance

Mark A. Buckingham, Leigh Aldous, et al.

JANUARY 07, 2022 ACS APPLIED NANO MATERIALS

Get More Suggestions >