FREEFORM FABRICATION OF ZINC AIR BATTERIES WITH TAILORED GEOMETRY AND PERFORMANCE

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Abstract

This work is focused on the freeform fabrication of complete zinc-air batteries. This method of production gives great freedom in the geometry and construction of the battery, allowing tailoring of the output characteristics, and the possibility of embedding a customized battery within a larger integrated freeform fabricated device. Our batteries utilize a gelling agent to prevent phase separation in the zinc anode and catalyst layers, permitting the use of nozzles down to 1.3mm in diameter. Polyvinyl alcohol is utilized for the separator layer, which replaces the unprintable paper separator used in commercial batteries. With various freeform batteries we have achieved a specific capacity of 60mAh/g of zinc, an average power 7.25mW, and continuous service life of 63h, all with a load of 100 ohms. The specific capacity of our freeform batteries is about 1 order of magnitude lower than that of commercial zinc-air batteries, although under different test conditions. We have investigated the effect of cell active surface area on performance for a cylindrical cell-geometry, and have produced a flexible, two-cell battery with unusual geometry. The tailoring of performance and geometry possible with freeform fabrication will be of great value in the design of optimized smart devices with unusual geometry, portable electronics, and prototypes.
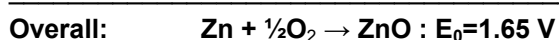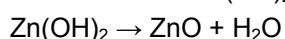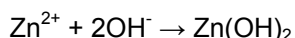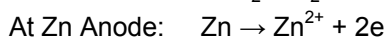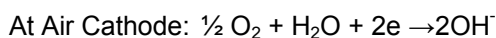
Introduction

Batteries are a necessary component in all electronic systems. By manufacturing batteries using freeform fabrication we open the door to creating completely freeform fabricated circuits as well as batteries integrated within other systems in a way not possible with current manufacturing techniques. Interest in flexible batteries is rising for embedded applications in smart cards and RFID (Akashi et. al, 2002). For example, PowerPaper Ltd. (2005) is manufacturing thin, flexible, alkaline cells through a lamination process. In addition, research in the area of direct-write electronics (Piqué and Chrisey, eds., 2002) has led to write-able electrochemical cells; however, these are embedded into integrated circuits using traditional, non-freeform, IC manufacturing. In prior work, we presented the first freeform fabrication of a complete, functional zinc-air battery (Malone et. al., 2004). Our past and current work remains the only example of the freeform fabrication of complete batteries. In the following, we present improvements to the materials and processes which have allowed us to freeform fabricate batteries in several geometries, and with tailored functionality. We developed new formulations for the zinc anode, catalyst, electrolyte, and separator materials which provide a satisfactory level of cell performance, while being easily deposited. We improved the manufacturing planning software of our system in order to accelerate and improve the quality of fabrication of multiple material devices such as batteries. We produced and tested a flexible, two-cell zinc-air battery with an unusual geometry, which demonstrates the design freedom which is possible using our freeform fabrication system. We have collected data on the effect of battery geometry on performance. To isolate the effect of geometry, we fabricated cylindrical batteries with differing surface areas and a standard mass of active material. The performance data from these will allow us to extend the predictive performance model of Mao and White (1992). A mature predictive

model and freeform fabrication capability will allow the size, shape, and performance of a cell to become free design parameters which can be customized for the specific geometry and functional requirements of a product. This will permit us to design and fabricate customized batteries for use in prototypes, portable electronics, and other novel applications. Battery design can be adapted to fit the existing product, rather than having the limited characteristics of commercial batteries dictate product design. An explanation of zinc-air chemistry will be followed by a presentation of the material formulations we have developed, the process of freeform fabrication for a battery, our testing procedure, and finally the batteries we have produced and their performance data.

Background

A cell is defined as a device that converts the chemical potential energy between its anode and cathode materials into electrical energy by means of redox reactions: reduction (electron gain) at the cathode, oxidation (electron loss) at the anode. A battery comprises one or more connected cells. The components of a zinc air cell are the anode terminal, cathode terminal, zinc anode, separator, catalyst, and electrolyte (Figure 3). The anode and cathode terminals are charge conductors which collect and transfer charge to external loads. The zinc anode and the oxygen cathode are the two key reactants in the cell. The separator provides electrical insulation between the anode and cathode to prevent internal shorting, but must be permeable to electrolyte to allow ionic current. The catalyst accelerates the rate of reaction in the cell, improving power output. The electrolyte, in this case aqueous potassium hydroxide, KOH, provides a medium for ionic transport within the cell, and a source of ions. The basic chemical reactions are:

At Air Cathode: $\frac{1}{2} O_2 + H_2O + 2e \rightarrow 2OH^-$
At Zn Anode: $Zn \rightarrow Zn^{2+} + 2e$
$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2$
$Zn(OH)_2 \rightarrow ZnO + H_2O$

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Overall: $\mathbf{Zn + \frac{1}{2}O_2 \rightarrow ZnO : E_0 = 1.65\ V}$

Formulation of Materials

Zinc anode paste

In creating the zinc anode paste we were required to balance several concerns. The zinc particles needed to be fully suspended in the electrolyte to provide a reliable flow rate without clogging or phase separation. We wanted to reduce hydrogen gas formation in the anode paste which causes problems with gas pockets in the loaded syringes and a loss of power output in a cell. We also need to select a zinc particle distribution which could be easily dispensed and give good cell performance. The resulting mixture for the zinc anode paste is given in Table I.

Table I : Zinc anode material formulation.

Material	% weight of zinc	% weight of total
Zinc Powder	100%	70.4%
8M aq. Potassium Hydroxide	40%	28.2%
Gelling Agent	2%	1.4%

The gelling agent was selected based on recommendations from Norteman (1979), Kerg (1981), Bahary (1986), Graham et. al. (1987), Bennett et. al. (1997), and Sumiya et. al. (2003), which give information about starch graft copolymers, carboxylmethylcellulose, and polyacrylic acid polymers. Multiple gelling agents from each of these groups were tested. The best results were obtained using a starch-based polymer with acrylonitrile side chains, commercially produced by B.F. Goodrich and known as Carbopol Ultrez 21. Graham and Goodman for Duracell Inc. (1987) note that "It has also been found that the use of (gelling agents of starch backbone and water soluble side chains) unexpectedly increases the practical discharge capacity of the anode while reducing the amount of cell gassing beyond that achieved through the use of previously known agents. Further, the internal resistance of the cell is not adversely increased." Later research by Bennett et. al. (1997) claims "the gelling agent acts to push zinc particles into spaces among its swollen particles to promote contact among the zinc particles, or between the zinc particles and the negative electrode current collector".

Table II : Performance of handmade cells with given amounts of gelling agent.

Gelling Agent (wt% of zinc paste)	0%	0.5%	1%	2%
Energy Output (J)	152.1	193.8	438.8	768.4
Average Power Output (mW)	0.53	0.54	1.43	2.25

Cells with differing gelling agent concentrations were tested, as shown in Table II, and the outcome supports the claim that greater amounts of gelling agent increase cell capacity and power output. Gelling agent amounts in excess of 2% gave zinc anode pastes of a doughy consistency and were very difficult to extrude. Therefore a gelling agent amount of 2% was chosen as this gave the best output performance and provided reliable extrusion.
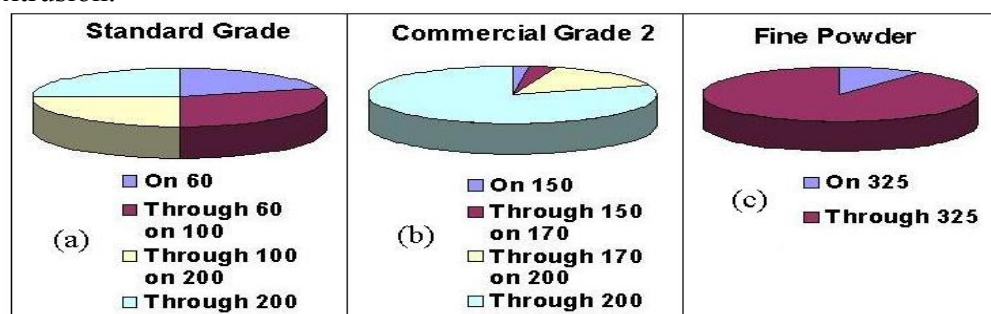

Figure 1 : Zinc particle size distributions: (a) Standard Grade zinc powder (Big River Zinc), (b) Commercial Grade 2 zinc powder (Big River Zinc), (c) laboratory grade zinc powder (Sigma-Aldrich).

The zinc particle size distribution was selected based on the recommendations of Chang et. al. (2003), Oyama et. al. (2004), and Durkot et. al. (2001), where the generally accepted particle sizes are between 50 and 325 mesh. Durkot states that the percentage of particles that pass through 200 mesh should be as much as 80 percent, and claims that cells with high proportions of fine zinc powder have increased performance especially in high drain usage. The patent offers the theory that this is due to particle-to-particle connectivity. Oyama states that both coarse and fine particles are needed, and that although increasing the amount of fine zinc particles improves discharge performance, it also increases generation of hydrogen gas through self-discharge. The Commercial Grade 2 distribution (Big River Zinc, Sauget IL) was chosen based on availability and ease of extrusion (Figure 1b). A greater percentage of fine particles,

passing through 200 mesh, permits the use of smaller nozzles without clogging. The Fine Powder distribution (Sigma-Aldrich, Inc.) has good extrusion performance; however, it displays significant hydrogen generation and causes problems with gas pockets in the extrusion syringes (Figure 1c). The Standard Grade distribution (Big River Zinc, Sauget IL) requires a larger nozzle size to extrude reliably (Figure 1a) and tests with handmade cells indicate lower cell performance than with the chosen distribution (Table VII).

Table III : Performance of handmade cells versus type of zinc powder employed.

Zinc Type	Fine Powder	Standard Grade	Commercial Grade 2
Gelling Agent (wt%)	2	2	2
Energy (J)	400.1	333.9	768.3
Ave. Power (mW)	1.75	0.92	2.29
Continuous Service (h)	62.7	100.2	94.4

We prepare the zinc anode paste by first weighing the desired amounts of zinc, electrolyte, and gelling agent on a laboratory balance. We thoroughly mix the zinc powder and powdered gelling agent by hand to ensure that the gelling agent is evenly dispersed. We add the electrolyte and again mix thoroughly by hand until no electrolyte settles out of the mixture. The electrolyte concentration we employ is 8M which is typically used in the art. The percent weight of electrolyte in the anode is 40% which falls under the recommendations given by Chang et. al. (2003) (35-40%), Urry (2001) (25-55%), and Bahary (1986) (30-40%). Then we allow the paste to sit for at least 12 hours in order for the gelling agent to fully hydrolyze. When the paste has fully hydrolyzed no electrolyte should have separated out from the zinc. We mix the paste thoroughly again by hand and load it into its syringe.

PVA Separator

We selected the materials for the separator based on the research presented by Treger et. al. (2003), who claim that a separator for an electrochemical cell can be formed *in situ* with a copolymer of polyvinyl alcohol and polyvinyl acetate. This technology proves particularly useful for application in freeform fabrication. This polyvinyl alcohol polymer, henceforth referred to as PVA, replaces the previous common technology of using unprintable paper (cellulose) separators. The PVA gel conforms to any geometry and when in contact with the electrolyte present in the zinc anode paste requires only 10 to 20 minutes to coagulate sufficiently to resume printing. The molecular weight distribution was changed slightly from the patent recommendation to favor a greater percentage of high molecular weight particles (Table VIII). We discovered that this change allows the separators to remain permanently flexible while not adversely affecting the cell performance. The gel is prepared by weighing the desired materials on a laboratory balance, mixing the dry materials, and slowly adding them to 60 degree water while stirring. The gel is mixed until the PVA crystals dissolve and then the gel is allowed to sit until the gas bubbles have escaped. The gel can then be loaded into the pistons for use.

Table IV: Polyvinyl alcohol (PVA) separator gel formulations.

Material	Original formulation (Treger et. al., 2003)	Permanently flexible formulation
Polyvinyl alcohol (M.W. 31k - 50k)	11%	10%
Polyvinyl alcohol (M.W. 85k - 146k)	3%	4%
Polyvinyl alcohol (M.W. 124k - 186k)	1%	2%
Deionized Water	84%	84%

Catalyst Paste

In creating the catalyst paste we need to adapt a typically dry mixture into one that could be extruded. Chang et. al. (2003) presents a catalyst formulation for metal air cells. We have adopted their recommendation for the ratios of dry materials (Table V).

Table V. Catalyst dry mixture

Material	wt%
Manganese dioxide	20
Oxidized Carbon Black	77
PTFE 5 μm powder	3

Table VI. Catalyst paste formulation

Material	wt%
Catalyst Dry Mixture	75
Carbopol Ultrez 21	7
8M aq. KOH	18

To suit our purposes for extrusion and freeform fabrication we adapted this dry mixture by adding gelling agent and electrolyte (Table VI). The electrolyte serves the purpose of binding the dry mixture into a paste and the gelling agent prevents against phase separation. The electrolyte in the catalyst paste also assists in the coagulation of the separator layer. The paste is mixed by hand and then allowed to stand for twelve hours in order to fully hydrolyze.

Case and Terminal Materials

Two additional materials are involved in the fabrication of batteries. A room-temperature vulcanizing (RTV) silicone (GE Silicone II, General Electric Silicones, Inc.) is used for the fabrication of the battery case and cap. This material is flexible, vulcanizes quickly (1-2 hours), is chemically resistant and inert, self-supporting, and easily deposited with 250μm resolution. The conductive terminals are produced using an RTV silicone filled with silver particles (SS-26, Silicone Solutions Inc.). This material is also chemically resistant and flexible, and bonds well to the silicone case to form a very robust conductor. The manufacturer claims an electrical resistivity of 5E-03Ω cm for the material.

Freeform Fabrication Process

The batteries are produced using a multiple-material freeform fabrication system (Figure 2). After the preparation of the materials, each material needs to be calibrated by varying the deposition control parameters until a uniform path of material is achieved. A three-dimensional CAD model of the desired battery is produced as an assembly. The model data is imported into the fabrication system software and material and fabrication properties are assigned to the parts of the assembly. Finally, the software generates a manufacturing plan from the design data, and executes the plan, using the syringe deposition tool and the various materials.
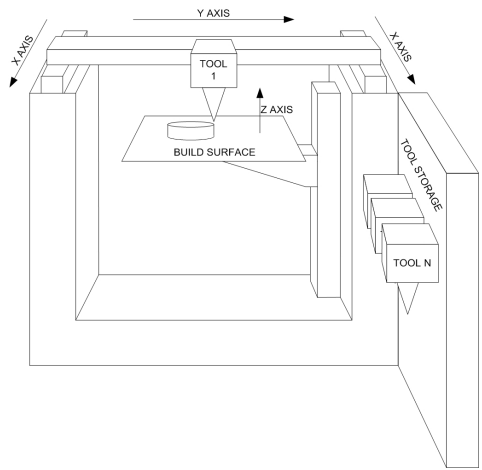
Figure 2. Schematic of our multiple-material freeform fabrication system

Each material allows a different degree of accuracy based on the smallest syringe tip that can be used to extrude reliably without clogging. The syringe tips are selected by hand extrusion testing with nozzles of decreasing diameter. The tips are disposable, and commercially produced by EFD Inc. Stainless-steel needles are used for multi-phase materials, and plastic tapered nozzles are used for high-viscosity materials (Table VII). Tapered nozzles are very prone to clogging with suspended solid-phase materials; however, they allow high-viscosity materials to be extruded through small orifices without excessive pressure. This allows us to obtain very high resolution with the silicone casing material, for instance.

Table VII : Design dimensions and syringe data of components of typical freeform fabricated battery.

Part	Material	Syringe Tip	Path Width (mm)	Diameter (mm)	Height (mm)
Casing	Silicone RTV	Red tapered plastic	0.254	28.5	9.25
Anode Conductor	Ag-filled silicone RTV	Amber stainless steel	1.3716	24.4	1.00
Zinc Anode	Zn anode paste	Green stainless steel	0.8382	24.4	5.00
Separator	PVA gel	Red tapered plastic	0.254	26.4	0.75
Catalyst	Catalyst gel	Purple stainless steel	0.508	24.4	0.75
Cathode Conductor	Ag-filled silicone RTV	Amber stainless steel	1.3716	24.4	1.00
Casing Cap	Silicone RTV	Red tapered plastic	0.254	28.5	0.75

Once suitable syringe tips are found, the deposition control parameters are identified for each material by iteratively depositing and measuring test patterns. The first phase of parameter identification involves setting the material flow rate and positioning system traverse rate in order to achieve uniform and consistent paths of deposited material under steady state conditions. The second phase then involves adjusting the acceleration, deceleration, start delay, and stop delay of the material flow and the acceleration and deceleration of the positioning system in order to minimize the start/stop transient variations in path geometry. Finally, the height and width of the

deposited road are measured. We enter the parameters and road measurements into the materials database of the freeform fabrication system where it is accessed for automatic fabrication process planning.

After the materials have been calibrated, the desired battery is modeled using a three dimensional mechanical CAD software package. Each component of the battery is modeled as an individual part, and then parts are assembled to form a complete battery model (Table VI). We take into account the calibrated road geometry for the various materials during the design process in order to ensure that the design is feasible. All design features must be larger than the measured dimensions of the path for that material. The basic cylindrical cell has a diameter of 28.5 mm and a height of 10 mm (Figure 3).
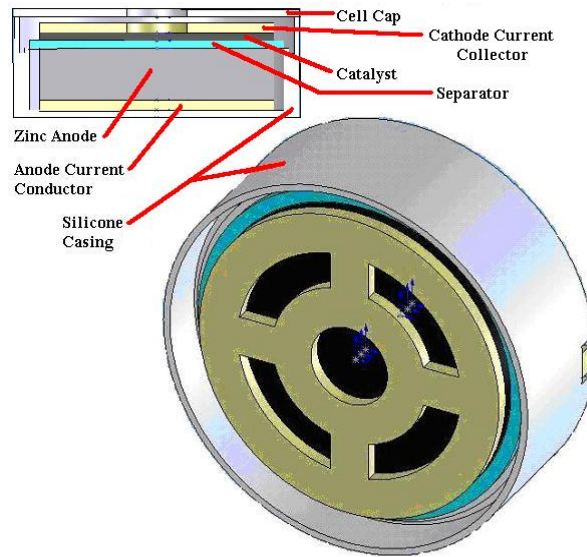

Figure 3. CAD model of standard cylindrical freeform fabricated battery; cutaway showing components (inset), and exterior view revealing cathode conductor, catalyst, and separator (cap hidden for clarity).

We import the design geometry data into the system control software of our freeform fabrication system. The software graphical user interface (GUI) is used to assign a material from the materials database to each of the component parts of the battery. Each material is loaded into a separate disposable syringe with the appropriate tip. The syringes are installed into cartridges, which are then manually mounted in the deposition tool as requested by the system control software during the course of the build. We also use the GUI to assign a sequential fabrication priority to each of the parts to take advantage of what we refer to as "backfill deposition" (Figure 4b). Our SFF system will fabricate higher priority parts of an assembly prior to lower priority parts, in violation of strict layered fabrication. The priority will be obeyed by the system except where doing so would violate the relationship of one part supporting another. Thus the silicone case of a battery can be given a higher priority than the materials to be deposited into it, and it will be completely fabricated to its full height before the deposition of any other materials into it begins. Backfill deposition allows the case to act as a container for materials which are not self-supporting, greatly improves the quality of deposition, and drastically reduces the number of material changes required which decreases build time.

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When fabricating a standard cylindrical battery, we set the battery case and the anode conductor to the same priority so the conductor can be build through an opening in the wall of the case for ease of connection (Figure 4a). The case is completed and the zinc anode layer and PVA separator layer are deposited using backfill (Figure 4b). The build is paused for 15 minutes to allow the PVA to react with the electrolyte and coagulate so that the separator will not be damaged by the remaining layers (Figure 4c). The catalyst, cathode current conductor, and casing cap layers are then deposited to complete the battery (Figure 4d). A standard cylindrical battery requires roughly 1.25 hours to be produced. In order to monitor the mass of active materials that is deposited into the battery, we mount a laboratory balance atop the build surface, and fabricate the battery onto a sheet of polyester film attached to the balance.
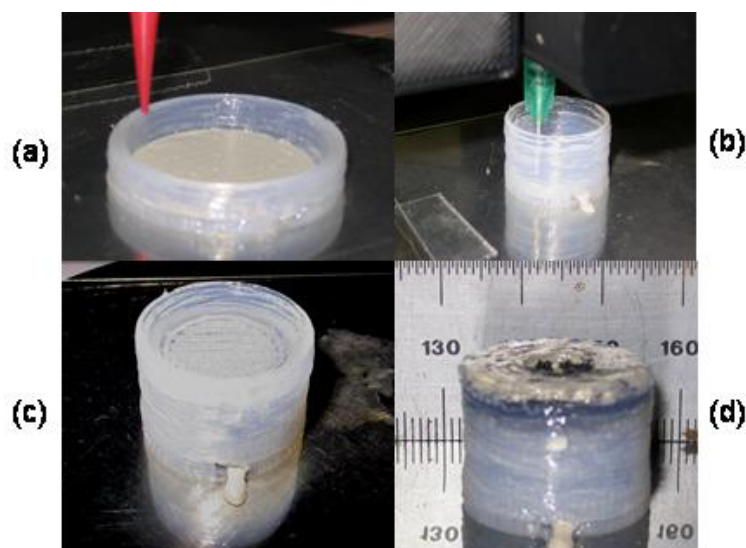

Figure 4. Freeform fabrication of a complete Zinc-air battery; (a) the fabrication of silicone case, (b) backfill deposition of the zinc anode, (c) coagulation of PVA separator layer, (d) completed battery.

Testing

We remove the battery from the freeform fabrication system and connect it to a data acquisition (DAQ) board. We connected the batteries to the DAQ board by pressing commercial stainless steel wires against the anode current collector tab and the top of the cathode current collector. The batteries are first allowed to reach a stable open circuit voltage before we place a load of 100 Ω in the circuit. We use software to record the voltage across the load resistor at a sampling rate of once a minute. When the cells fall below 0.1 volts we stop the recording and remove the batteries.

Results and Discussion

The resultant discharge curves of the freeform fabricated batteries are shown in Figure 5. The curves are characteristic of zinc air batteries which have a long period of constant voltage followed by a rapid drop-off. As expected the triple cell area has the highest voltage and operating current, however it has the shortest lifetime. The standard cell shows a slightly lower voltage and operating current, and a slightly longer lifetime than the triple-area cell. The half area cell has a much lower voltage and operating current, however it achieves a lifetime twice that of the standard cell.

Based on these results, we can estimate the specific current capacity (Figure 6), service lifetime, and average current (Figure 7) of a freeform fabricated battery of a given intermediate active surface area. A smaller surface area gives a lower current because there is less area for reactions to take place. As the surface area increases the current reaches a limiting value for a given load. The open circuit potential for a zinc-air cell is about 1.4V, though the nominal loaded voltage drops to about 1.2V and higher current densities result in even lower output voltages. Mao and White (1992) explain the drop to 1.2V as the initial depletion of free OH⁻ ions from the electrolyte, and the larger drop with increased current density as reaction-rate limitation. In our testing, cells with greater surface area achieved higher operating voltages, although none achieved the 1.2V nominal voltage. This suggests that we are operating at too high of a current density for the design or materials employed in our cells. In addition, the greater the exposed surface area the shorter the lifetime, implying that dehydration may also be a limiting factor.
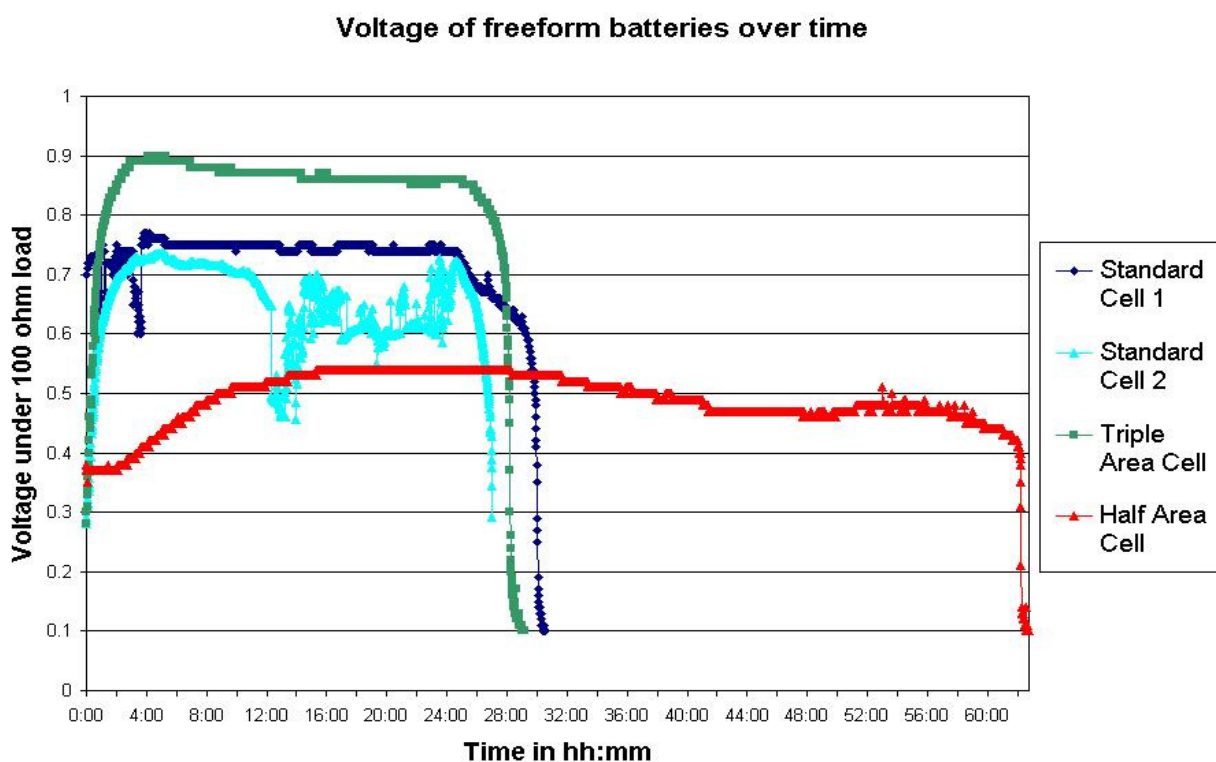

Figure 5. Discharge curves for cylindrical batteries of three different active surface areas.
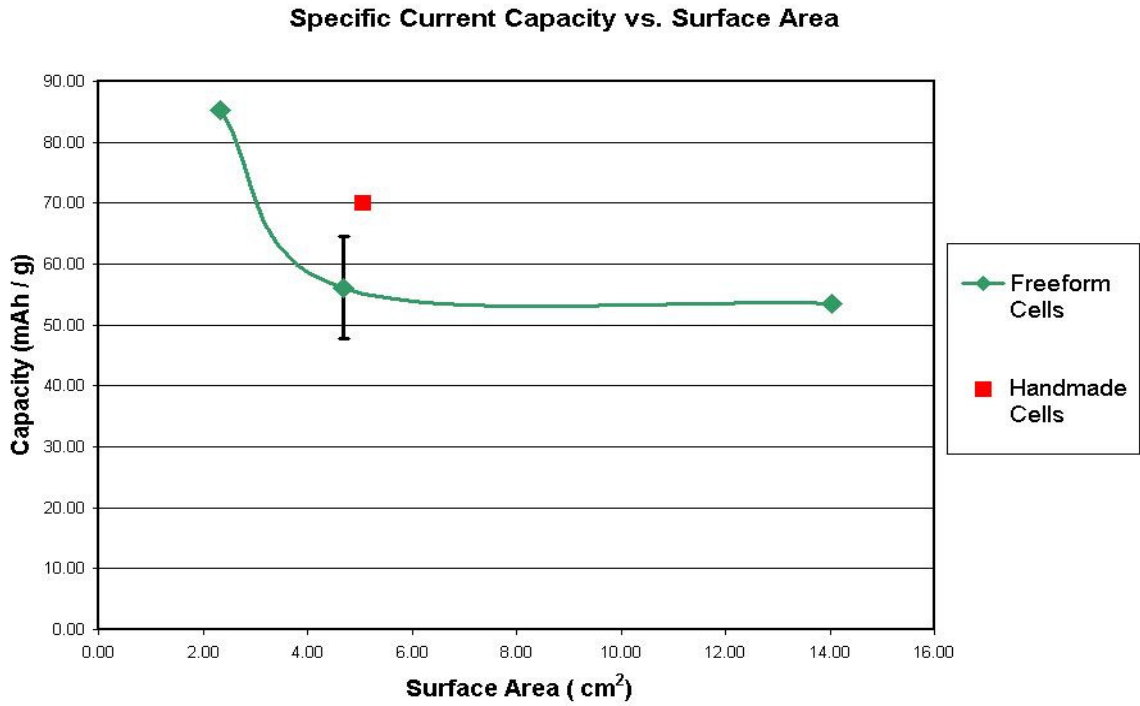
Figure 6. Specific current capacity (to mass of zinc in anode) of cells versus their active surface area. Error bars are 1 standard deviation for sample size of 2.
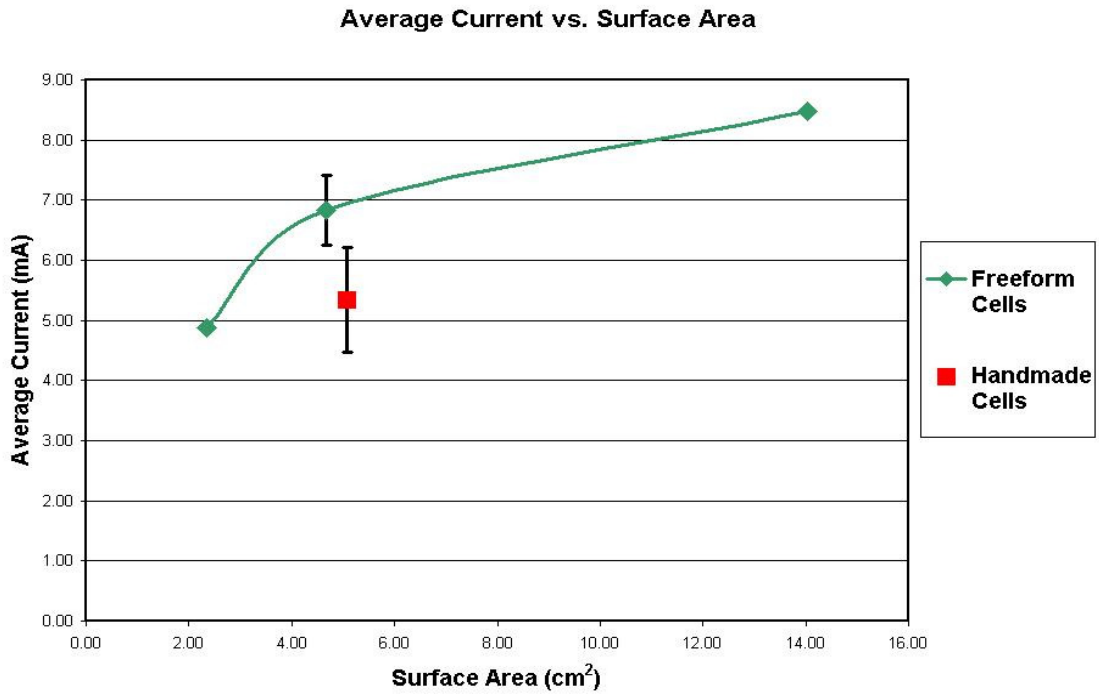

Figure 7.Average current from cells over service life into 100 Ohm load versus surface area.

	Commercial	Freeform Fabricated				Handmade	
	Eveready AC675 (2004)	Basic 3	Basic 4	Triple 1	Half 1	HM1	HM2
Open Circuit Voltage (V)	1.40	1.38	1.09	1.29	1.29	1.33	1.34
Cont. Service Life (h)	302 (@16h/day)	27.48	30.06	28.20	63.00	38.90	69.61
Fabrication Time (h)			1.25	1.43	1.83		
Energy Output (J)	2996.6	416.59	570.63	736.07	543.55	760.27	576.00
Ave. Power (mW)	2.76	4.28	5.28	7.25	2.41	3.56	2.29
Ave. Current (mA)	2.1	6.42	7.25	8.48	4.87	5.96	4.72
Capacity to .4V (mAh)	635	176.45	217.83	239.27	306.88	231.80	328.56
Mass of Anode (g)	~ 1	4.99	4.99	6.36	5.1	23.30	22.90
Mass of Zinc (g)	<1	3.51	3.51	4.48	3.6	16.40	16.12
Surface Area (cm^2)	1.05	4.68	4.68	14.04	2.34	5.07	5.07
Specific Energy (kJ/kg)	1577.16	118.59	162.44	164.40	151.09	157.74	145.80
Ave. Power/Area (mW/cm^2)	2.63	0.91	1.13	0.52	1.03	0.77	1.03

Table VIII gives a full listing of all result data and calculations. Data from zinc air button cells is listed for comparison. The comparison to commercial cells is not accurate, in that commercial batteries are tested with a load of 625Ω and therefore discharge at a lower current density. This may explain some of the disparity in performance. Improvements to cell capacity will include a humidity control layer, such as PTFE dispersion, design changes to reduce electrolyte evaporation, and adjustments to the separator layer to prevent the zinc anode from becoming exposed.

To fully utilize the possibilities of freeform fabrication, we have designed and produced a flexible, two-cell, zinc air battery with an unusual geometry. We chose a U-shape where the layers were organized horizontally instead of vertically to allow air flow to both catalyst layers, as shown in the CAD model (Figure 8a). The completed cell measures 11 centimeters long and 8 centimeters wide (Figure 8b). The cell provided an open circuit voltage of 2.5 V, clearly indicating the functioning of both cells in the two-cell configuration. After overnight testing with a 100Ω load, the cell still produced an open circuit voltage of 1.41 V. The loss is likely due to breakage in the separator layers which allows internal shorting. Increasing the thickness of the separator layers should eliminate the internal shorting. The geometry of the battery and the material formulations allow the battery to be flexed (Figure 8c) and the battery maintains the 1.4V output even when flexed (Figure 8d). This demonstration shows only one example of the geometries that are possible using a freeform fabrication system.
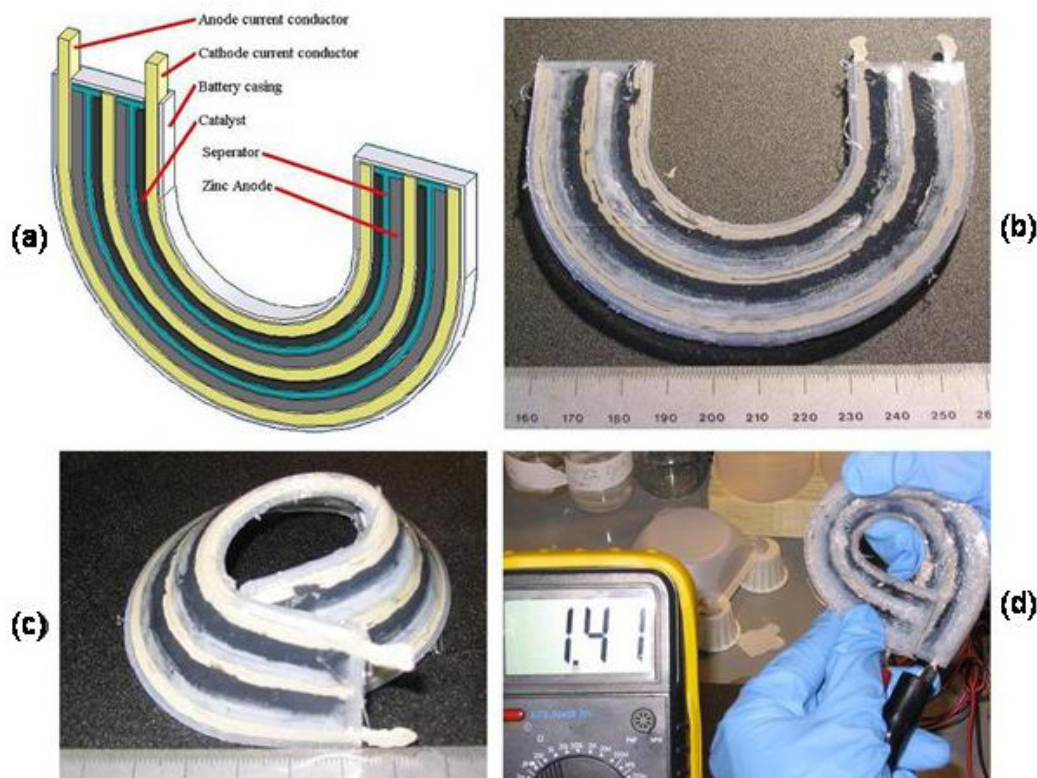
Figure 8. (a) Labeled CAD model of two cell U-shaped battery, (b) completed battery, (c) demonstration of the flexibility of the battery, (d) voltage after testing.

Conclusion

Through an extensive set of experiments with handmade zinc-air batteries, and taking advantage of the commercial research represented by numerous patents on traditionally manufactured batteries, we have developed new formulations for the zinc anode, cathode catalyst, and separator materials which are suitable for freeform fabrication. We have produced and tested a flexible, two-cell battery with an unusual shape that shows the type of geometric and functional customization that freeform fabrication brings to the manufacture of batteries. We have collected performance data for a series of freeform fabricated batteries of identical design but varied diameter. This data allows the estimation of the performance of a battery of a similar proposed design prior to fabrication. We are continuing to collect data from batteries of widely varying designs to more fully identify the effects of geometry on freeform fabricated battery performance. Using our data for freeform fabricated batteries, we will extend the predictive model of Mao and White (1992) to cover more complex geometries and multi-cell batteries. This will lead to a true predictive performance model which can be used to design geometrically and performance-optimized zinc-air batteries for incorporation into many different electrical applications.

References

Akashi, H., K. Tanaka, et al. (2002). "A flexible Li polymer primary cell with a novel gel electrolyte based on poly(acrylonitrile)." Journal of Power Sources **104**(2): 241.

Bahary, W. S. (1984). Cell gelling agent. United States Patent 4,563,404. United States of America, Duracell Inc.

Bennett, P. S., K. H. Kenyon, et al. (1996). Gelling agent for alkaline electrochemical cells. United States Patent 5,686,204. United States of America, Rayovac Corporation.

Chang, H. and I. Chi (2001). Battery and method of making the same. United States Patent 6,593,023. United States of America, The Gillette Company.

Durkot, R. E., L. Lin, et al. (1997). Zinc electrode particle form. United States Patent 6,284,410. United States of America, Duracell Inc.

Eveready Battery Company, Inc. (2004). Engineering Datasheet ENERGIZER NO. AC675, http://www.energizer.com.

Graham, T. O. and J. T. Goodman (1980). Electrochemical cells having a gelled anode-electrolyte mixture. United States Patent 4,681,698. United States of America, Duracell Inc.

Kerg, C. A. (1980). Alkaline-MnO.sub.2 cell having a zinc powder-gel anode containing starch graft copolymer. United States Patent 4,260,669. United States of America, Union Carbide Corporation.

Malone E. and H. Lipson, (2004) "Freeform Fabrication of Electroactive Polymer Actuators and Electromechanical Devices", 15th Solid Freeform Fabrication Symposium, Austin TX, Aug 2004, pp.697-708.

Malone, E., K. Rasa, et. al. (2004). "Freeform Fabrication of Zinc-Air Batteries and Electromechanical Assemblies." Rapid Prototyping Journal: **10**(1): 58-69.

Mao, Z. and R. E. White (1992). "Mathematical modeling of a primary zinc/air battery." Journal of the Electrochemical Society **139**(4): 1105.

Norteman, W. E. (1978). Alkaline-MnO.sub.2 cell having a zinc powder-gel anode containing P-N-V-P or PMA. United States Patent 4,175,052. United States of America, Union Carbide Corporation.

Oyama, A., T. Odahara, et al. (2002). Process for producing zinc or zinc alloy powder for battery. United States Patent 6,746,509. United States of America, Mitsui Mining & Smelting Company, Ltd. (Tokyo, JP); Matsushita Electric Industrial Co., Ltd. (Osaka, JP).

Piqué, A. and D. B. Chrisey, Eds. (2002). Direct-write technologies for rapid prototyping applications: sensors, electronics, and integrated power sources. San Diego, California, Academic Press.

PowerPaper. (2005). "Battery Specifications (http://www.powerpaper.com/3_technology/batteryspecs.htm)." Retrieved 7/15/2005, 2005.

Sumiya, T., M. Koike, et al. (2001). Gelating agent for alkaline cell and alkaline cell. United States Patent 6,667,133. United States of America, Sanyo Chemical Industries, Ltd. (Kyoto, JP).

Treger, J., S. Sargeant, et al. (2000). Alkaline cell with cathode surface protector. United States Patent 6,514,637. United States of America, The Gillette Company.

Urry, L. F. (1998). Method for producing an electrode containing electrolyte-absorbed polymer particles. United States Patent 6,280,877. United States of America, Eveready Battery Company, Inc.