**Embeddable Batteries: Taking Shape**

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Just as embedded electronics are becoming an integral part of sensors, unmanned aerial vehicles, and a number of other instruments, so are embedded power sources. In a larger-scale application such as power generation, existing silicon-based and futuristic high-efficiency thin-film solar cells will have high-energy-density and high-power-density thin-film batteries for energy harvesting, storage, and delivery. This article describes some of the recent developments at APL in the area of three classes of emerging battery technologies. In one class, the batteries are embedded into the instrument by fabricating them in conformal shapes. In the second class, the objective is to grow them on surfaces that serve as the skin of the solar cell or the skeleton of the instrument. In the third approach, using emerging nanotechnology, battery chemicals are encapsulated inside metal nanotubes that are grown in situ in thin-film polymer sheets that are subsequently bonded together into batteries.

**INTRODUCTION**

There is a great need for infusing power sources directly into lightweight, thin-film polymer- and silicon-based electronic structures. State-of-the-art electronic systems are at submicrometer-scale, embedded within control systems and mechanical devices, and require only microwatts to milliwatts of power to operate. Today, from prosthetic arms to munitions and from wearable electronics to sensor networks, most emerging technologies use embedded electronics, processors, and other complex circuits. In most devices, including the prosthetic arms being developed by APL for the Defense Advanced Research Projects Agency (DARPA), the need to embed thin-film power sources as an integral part of the thin-film electronics is an inevitable consequence of the need to manage mass, volume, internal heat, and other logistics. In the area of solar cells,
using existing technology, a 10,000-ft² area such as the rooftop of APL’s library or cafeteria is capable of generating 57 kW of power and 458 kWh (458 units) of energy per day. All of this energy can be stored in batteries integrated with the solar cells as a thin film spread 0.15-inch thick over 10,000 ft². (Assumes solar cell converted power density as 100 W/m², specific energy of the rechargeable battery as 100 Wh/kg, and density of the battery as 4 g/cm³.)

Embeddable, thin-film polymer-based batteries have another important advantage over the commercial fixed-shape power sources. They can be prefabricated as sheets and then cut and pasted according to the available space. Over the past 4 years, APL has been designing and testing novel-shaped batteries for our customers. There has been an increasing demand for batteries that fit the space, power, and energy demands of specific devices, as opposed to the conventional ways of allotting space within a device for an existing commercial battery.

**WHY ANOTHER BATTERY?**

Commercial off-the-shelf batteries have some limitations for use in emerging devices such as micro-unmanned aerial vehicles (UAVs) and microsensors:

- Their internal structures and chemistry cause their internal resistance to be too high under high discharge conditions;1-4,6 and
- Those that are designed for higher discharge rates are usually too heavy to be carried by micro-UAVs, sensor networks, birds, and bumblebees.

Power demand in UAVs may fluctuate by a factor of 3 or more; in sensor networks, the fluctuation may exceed a factor of 10 or more. For example, a sprinting micro-UAV may need three times the 5–10 W of power it needs while hovering, or a transmitting sensor 30 times more power than while hibernating. In bird- and beelike arrangements, the space available inside them may be incompatible with the shape of commercial batteries; instead, there may be a need to reshape the battery’s form factor to be in compliance with the shape and size of the device. The APL design attempts to overcome all of these problems and meet the needs of today’s customers. The APL microbatteries are called Power Beads.

Our goal has been to design batteries that exhibit the following characteristics:

- Conform to the available space
- Bond directly with polymer films that may carry electronic circuits
- Have facile integration with silicon surfaces and, therefore, with electronic parts
- Handle order-of-magnitude fluctuations in load without the need for power-conditioning circuits.

This article describes developments made or in progress since early 2005 in custom-shaped batteries in the following formats:

- Beads, curves, and other irregular shapes, collectively called Power Beads, in a polyurethane housing
- Thin (500-µm) polyurethane sheets
- Thin (10-µm) polycarbonate membranes
- Nanotubes embedded in thin polymer films and silicon wafers

**THE POWER BEAD**

Power Beads are designed with three major criteria:

1. Maximize the volumetric energy density.
2. Shape to fit into the available space or cavity in the device, which is different from the rigid shapes of commercial batteries.
3. Generate higher pulse power than what one can get from commercial microbatteries of comparable volume or mass.

We utilize two nonconventional paths to achieve these goals:

1. Use polymers as the shell or housing for the battery. Polymers have a lower density; therefore, the housing material contributes a smaller mass than do the metals that are most commonly used in commercial batteries. Polymers also can be cast into required shapes.
2. Keep the cross-sectional area of the battery as large as possible; this keeps the internal resistance small, allowing discharge of large currents without excessive polarization of the cell voltage.

These apparently simple ideas generate potential difficulties in their implementation. Note that batteries have several different types of chemicals inside them, mostly oxidizers, reducers, and corrosive electrolytes. The oxidizers and reducers tend to react with their surroundings, including many polymers. Because the quantity of chemicals inside a microbattery is only in the microgram to milligram range, even a small loss to reactions with their surroundings would result in substantial loss of stored energy. The electrolytes are organic or inorganic salts dissolved in a few microliters of a solvent. If the solvent diffuses through the battery shell or evaporates, which is easier if the shell is a polymer, then the internal resistance of the battery will rise, rendering the battery unusable. Commercial battery manufacturers have solved both problems: they use chemical-resistant metal alloys for the housing that also are impervious to water and other solvents. We have yet to store the Power Beads in excess of 6 months before discharge; characterizing them for longer shelf life will require further work.
In Power Beads, the housing material is a hard polyurethane, which is lightweight and easy to cast; alternatively, the housing can be made of soft-body materials such as polyvinylchloride (PVC) or silicone. The battery chemistry within the shell is silver oxide–zinc; one also could use most other nonlithium chemicals commonly available for energy storage and discharge.

**Lightweight Housing for the Power Bead**

In the examples shown in Fig. 1, the shell or the housing for the Power Bead was made by casting a high-durometer thermosetting polyurethane in the required shape. Thermosetting polymers usually tend to be rigid. For less-rigid structures, one could use polymers based on silicone or a thermoplastic such as PVC. Note that the casing may contain one or more parts that are assembled together to obtain a required shape and size. Examples of the Power Bead shapes shown in Fig. 1 include cylinders and curves; in addition, one can shape them as sheets and strings.

**Advantages of Using a Polyurethane Housing**

The advantages of using a polyurethane housing are as follows:

- Being a low-density material (polymer density of <2), the housing is lighter than its metal and alloy counterparts (density of >7).
- Casting polymers requires simpler tools than casting metals; therefore, it is easier to make housings of varied shapes.
- Furthermore, polymers can be cast, under ambient conditions, into an available space inside a device; with metals, in situ casting is nearly impossible.
- Polyurethane, in particular, is relatively inert toward the chemicals, including the electrolyte and energy-storing materials found inside batteries.
- Being a good electrical insulator, the polyurethane housing eliminates the possibility of short-circuiting.
- Within the same housing, it may be difficult to combine metals of different elements because of the possibility of galvanic corrosion; by contrast, it is easy to assemble and seal a polymer housing by using other thermosetting polymers.
- The main deficiency of using a thermosetting polymer for housing is its mechanical strength. It does not have good mechanical strength in most forms and shapes.

**Discharge Characteristics of the Power Bead Button Cell**

The mass and volume of the Power Bead Button Cells (PBBCs) shown in Fig. 1 are, typically, 0.85 g and 0.3 cm$^3$, respectively, which are comparable with commercial button cells such as Duracell’s D389/390 and Maxell’s SR1130S. Figure 2 shows the discharge characteristics of the PBBCs across a constant load (1500 Ω) at 20°C; the discharge characteristic of the Duracell D389, also at 20°C, is provided for comparison. Table 1 provides the gravimetric and volumetric comparison of the PBBC with different commercial models.

There are two major differences between the discharge behavior of the PBBC and its commercial counterpart, the D389 (Fig. 2):

1. The PBBC has 30% more ampere-hour capacity (90 mAh versus 70 mAh for the Duracell D389).
2. The PBBC discharges in two steps. The first step is at 1.8 V, and the second is at 1.5 V. The commercial battery, on the other hand, discharges at 1.5 V.
The reason for both differences is the same: the PBBC is filled with silver (II) oxide, Ag(II)O, which first discharges to Ag(I)O (step 1) and then to Ag (step 2). Commercial batteries, in contrast, are filled with Ag(I)O; hence, they discharge in a single step, closer to 1.5 V. Historically, manufacturers preferred the batteries to discharge in a single step to be compliant with their electronics that operated at a fixed voltage with very little variability. However, modern electronics have a wider compliance range; thus, a two-step discharge may be acceptable. The advantage of using Ag(II)O is that the battery has a higher storage capacity for the same comparable volume.

The PBBC has a higher energy density (both volumetric and gravimetric) than the Duracell D389. The use of polyurethane as the housing material also provides the PBBC with a mass (or weight) advantage over the commercial battery: the gravimetric energy density of the PBBC also is 30% better than the Duracell D389. To “catch up” with the ampere-hour capacity of the PBBC, the commercial batteries will have to nearly double their volume, as in the cases of the Maxell SR44 and Duracell S76 (also included in Table 1).

**Discharge Characteristics of the Power Bead Curve Shaped**

When discharged at the rate of 0.1 mA at 20°C, the Power Bead Curve Shaped (PBBS) (shown in Fig. 1a) provides a current capacity of 11.5 mAh, and, at a much higher rate of discharge of ~1 mA, the same battery provides 7.3 mAh. By comparison, Maxell’s SR512SW has a current capacity of 11.5 mAh, but only when discharged at a 20-µA rate; discharging at 1 mA yields only 2.5 mAh, resulting in a loss of >75% of its capacity. (The discharge data for the PBBC and SR512SW are available and will be provided upon request.) Furthermore, the PBBC can be pulse discharged at rates that one would consider to be relatively high for microbatteries without concern for significant polarization effects (loss of cell voltage), as may be seen from the data in Fig. 3.

**THE POLYURETHANE SHEET BATTERY**

In this battery, the individual electrodes are made by using flexible polyurethane sheets that typically are <1 mil (~15–20 µm) thick and bonded together using a process known as B-staging. The process involves making each electrode by mixing the urethane monomer with the necessary battery chemical and additives, initiating the polymerization process, but not allowing it to fully polymerize. Next, the partially cured electrodes (anode and cathode) and the separator are stacked together and allowed to continue through the rest of the polymerization process. During the course of this process, all three layers (anode, separator, and cathode) tend to bond with each other to form a 55-µm-thick cell. Typically, these cells are made as sheets and then cut to the required size and shape.

Figure 4 shows an image of a polyurethane sheet battery (PSB). The active materials, once again, are

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**Table 1. Mass, volume, current-capacity, and energy-density specifications for the PBBC and comparable commercial batteries.**

<table>
<thead>
<tr>
<th>Battery type</th>
<th>Mass (grams)</th>
<th>Volume (cm³)</th>
<th>Current Capacity</th>
<th>Energy Density</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Volumetric (Ah/L)</td>
<td>Gravimetric (Ah/kg)</td>
</tr>
<tr>
<td>PBBC, 90 mAh (discharged across 1500 Ω)</td>
<td>0.9</td>
<td>0.300</td>
<td>300</td>
<td>100</td>
</tr>
<tr>
<td>Maxell SR1130S and Duracell D389/390, 70 mAh</td>
<td>1.2</td>
<td>0.327</td>
<td>230</td>
<td>62.5</td>
</tr>
<tr>
<td>Maxell SR44 and Duracell D357/MS76, 165 mAh</td>
<td>2.3</td>
<td>0.540</td>
<td>305</td>
<td>72.0</td>
</tr>
</tbody>
</table>

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silver oxide and zinc. Electron conduction is achieved either by adding nickel-coated carbon nanofibers or by reinforcing the polymer with micrometer-thick metal mesh. An added advantage of the additives (nanofibers and metal mesh) is that they tend to increase the mechanical strength of the polyurethane sheets. The discharge characteristic of the battery with a 15-kΩ load resistor is shown in Fig. 5. Note that, in general, the silver oxide–zinc is a unique system in which the internal resistance decreases as the battery discharges. This decrease happens because of the formation of metallic silver as the electrochemical reaction during the discharge transforms silver oxide into silver. In the PSB system, between 5% and 70% of the discharge time, the decrease in the internal resistance manifests as increasing cell voltage and sharp, comb-like pulses. A constant, 20-mA, 100-ms pulse discharge of a similar battery is shown in Fig. 6.

The PSB has potential multifunctional properties and can double as a polymer structure that conducts on both surfaces while functioning as a battery. In its role as a battery, a PSB with 1-cm² area will generate 1.25 V at 80-μA constant discharge and 1.3–1.4 V under 20-mA pulse discharge; the corresponding power generations are 100 μW and 25 mW, respectively. Note that the discharge voltages of PSBs are much smaller than the 1.45–1.75 V observed in the PBBC battery. The lower voltages in the PSB are probably attributable to the mild reduction of silver (II) oxide by a chemical component in the precured urethane mixture into silver (I) oxide, similar to the known procedure used to make AgO behave like Ag₂O in primary silver oxide–zinc batteries.⁸

**NANOTUBE BATTERIES**

Nanotube batteries are next-generation batteries currently under development at APL. These batteries are based on engineering designs that are different from the ones described earlier. The following description of the nanotube battery is mostly conceptual; only a few

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**Figure 3.** Pulse discharge characteristics of a PBCS at 10 mA (a), a PBCS at 20 mA (b), and a Maxell SR512SW at 8 mA (c). Note that the commercial battery polarizes far below 1.4 V. The cut-off voltage, 1.4 V, is shown as a horizontal dashed line.

**Figure 4.** Photograph of two 1-cm², 53-μm-thick polyurethane batteries.

**Figure 5.** Discharge characteristics of the 1-cm² PSB, shown in Fig. 4, across a 15-kΩ resistor. In this case, nickel-coated carbon nanofibers provided electrical conduction. The cut-off voltage, 1.0 V, is shown as a horizontal dashed line.
batteries of this design have ever been made, and more refined fabrication and characterization are ongoing.

Metal Nanotubes

Before going into the details of the nanotube battery, it is worth discussing the metal nanotubes (MNTs) used in the construction of the nanotube battery. The word "nanotube" commonly evokes the phrase carbon nanotube (CNT). The nanotube batteries described here are made using MNTs and are not associated with CNTs. In nanotube batteries, MNTs are used as the housing material to encapsulate battery active (energy-storing) chemicals. CNTs are too thin, and their internal diameters are too small, to serve as a nanotube battery; some battery manufacturers have attempted to use CNTs as additives in their battery chemicals to improve conductivity, with little improvement over the conventional additive, carbon black. Lithium-ion battery researchers also have studied the potential use of (lithium-interstitial) CNTs as an alternative, high-capacity active anode material compared with the conventional active anode material graphite. Although CNTs were found to have very high initial capacity (~1000 mAh/g compared with graphite’s theoretical capacity of 372 mAh/g), the CNTs exhibited severe capacity fading after several charge/discharge cycles.

Thin-Film Nanotube Batteries

The nanotube battery contains thin-film porous polymers or silicon as the electrodes and MNTs as the housing to encapsulate the active (energy-storing) chemicals. The electrode preparation process is elucidated in Fig. 7. The starting material is a 10-μm-thick porous polymer membrane, and the goals are to (i) fill up the pores with energy-storing, battery-active chemicals and (ii) enable the polymer to conduct electrons to and away from the chemicals. The first step in the process is to metallize one side of the membrane for conduction. Next, the pore walls are metallized, also for conduction; the metal chosen for conduction is electrochemically nonreactive. The pores in the polymer membrane typically are straight, cylindrical, and several micrometers in diameter. After metallization, if the membrane were dissolved and removed, what remained would be a “forest” of metal nanotubes. Figure 7a shows the image of such a forest. A single (5-μm-diameter, 11-μm-tall) MNT from this group is magnified further in Fig. 7b. In this example, the MNTs were grown taller than the thickness of the membrane.) Finally, each metallized pore is filled with an active chemical—such as nickel hydroxide, silver oxide, zinc, lithium, etc.—and partially capped to prevent their leakage, as shown in Fig. 7c. The porous space above the nanotubes is filled with a gel or solid electrolyte. A polymer electrode with nanotubes holding a battery chemical constitutes an anode or a cathode. A cell (Fig. 7d) is formed by layering an anode on a cathode and sealing the edges. Figure 8 shows a 1-inch-diameter MNT silver-zinc cell (left) and its output voltage (right).

Note that, in this design, there is no separator between the anode and cathode: Conventional designs of electrodes used in commercial batteries include a metal or graphite as the support structure that doubles as current collector. The nanotube battery, on the other hand, uses a polymer as the support structure that is only partially coated with a metal (for collecting electrons). The sides of the anode and the cathode that touch each other contain the electrolyte; more importantly, they are devoid of the electron-conducting metal (current collector), eliminating the possibility of short-circuiting, as well as the need for a separator.

Conventional batteries also use matrices or support structures that are usually metals or carbon-based materials. They generally contribute >50% of the mass and volume of the battery. Because the conventional matrices do not themselves store energy but only support the chemicals that do, they add to the deadweight and volume, diminishing the energy density and specific energy of the batteries. Our nano-design replaces the conventional support structure with highly porous, low-density matrices such as polycarbonate, nylon, aerogel, and silicone. Most polymers are inherently low-density materials, and making them porous further reduces their mass. They can be made in large sheets, cut to shape, and bonded by using conventional techniques. Absence of a separator in the nanotube battery design provides the new batteries with a greatly reduced internal resistance. Because the diameter of each pore, where the energy-storing chemicals reside, is on the order of nanometers...
Figure 7. Scanning electron microscopy images of a highly magnified (>1000×) section of an MNT battery electrode. (a) Ni nanotubes grown in situ in a 10-μm-thick polymer electrode. (b) A magnified view of one of the nanotubes, after etching the polymer away. (c) Initial stages of filling the nanotubes with an energy-storing battery chemical. (d) Cross section of a nanotube silver-zinc battery.

Figure 8. A 1-inch-diameter silver-zinc MNT battery (a) providing 1.288 V under discharge at the rate of a few microamperes (b).

to micrometers, all of the energy-storing chemical particles are in close proximity to an electron conductor. The proximity to an electron conductor further reduces the internal resistance of the battery.

SUMMARY

This article summarizes the ongoing effort at APL to develop shape-conforming and thin-film high-power and high-energy batteries. The PBBC system of batteries that are cast into polyurethane housings occurred early in the development (2005–2006) and has a fairly matured foundation. It is a primary battery (nonrechargeable) that has undergone relatively long-term studies, extending up to 6 months from the day of construction. This custom-made system can be produced in various shapes in addition to the ones shown in Fig. 1.
The PSB batteries (2006) were made as 50- to 60-μm-thin nonseparable layers of polyurethane. The discharge data of this system (shown in Figs. 5 and 6) were obtained 1 or 2 days after construction for the purpose of proof-of-concept. Polyurethane has the potential to be used as a multifunctional material and can double as a structural component of the overall device/system. It is a useful power system for sensors that run on micro-watts of power and transmitters that require milliwatts of pulse power.

The nanotube batteries are the most recent ones (2008) and are in the early stage of development. Here, nanotechnology provides an opportunity to completely redesign batteries in several ways, especially to minimize the internal resistance and increase energy-conversion efficiency. Using low-density materials such as polymers or thin silicon membranes with nanopores for electrodes alters the approach to designing a battery in ways that could not be imagined in the past.

In the past, from the sintered-plate approach in Edison’s NiCad to graphite-intercalated design in modern-day lithium-ion, the design mechanics have been nearly the same, and most of them generate heat energy at an equivalent of ≥20% of their electric energy; in extreme cases, hermetically sealed batteries can explode as a result of heat-assisted pressurization of their internal volume. All of the previous designs also restrict the amount of useful energy to <25% of the theoretical capacity. Furthermore, instruments are required to be designed with a separate space to contain the power source and connect it to the instrument through wires and connectors.

This work demonstrates that it is indeed possible to integrate the battery with the structure of the electronics and the instrument. As an example, the thin-film battery in nanotubes could be shaped as the wing or fuselage of a micro-UAV or other unmanned autonomous system. Sequestering the materials in individual nanotubes allows maximum use of the energy-storing chemicals. A design without a separator (between the anode and cathode) reduces the internal resistance, thus allowing the battery to generate more useful electric energy and less waste heat.

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