Ultra-Thin, Flexible Solid-State Battery with Integrated Solar Energy Harvesting

Brian Berland¹, Calvin Sprangers¹, Alvin Compaan², Victor Plotnikov², David Carey³, John Olenick³, and Kathy Olenick³

1-ITN Energy Systems, Inc., 8130 Shaffer Parkway, Littleton, CO, USA 80127
2- Lucintech, Inc., 1510 North Westwood Avenue, Toledo, OH, USA 43606
3- ENrG, Inc, 175 Rano St., Suite 101, Buffalo, NY, USA 14207
bberland@itnes.com / 1-303-285-5107

Abstract: With funding from the FlexTech Alliance, ITN Energy Systems and ENrG Inc. have demonstrated promising new thin, solid-state lithium rechargeable batteries (SSLB) capable of providing the high power and energy required for many flexible electronics, wireless devices/sensors, wearables, medical devices, unmanned vehicles, portable power, etc. Combining ITN’s SSLB with ENrG’s ultra-thin flexible ceramic solves the capacity and packaging issues that have thus far limited the thin film battery technology to niche applications. With a capacity up to 100 mAh in a thickness less than 250 microns, including hermetic packaging, the new SSLB enables energy density greater than 1,000 Wh/l while maintaining the benefits of enhanced safety and durability provided by the all solid state chemistry. Results are also presented for a new Flexible Integrated Power Pack (FIPP) that adds in-field solar recharging by combing the SSLB with Lucintech’s high efficiency CdTe solar cells.

Keywords: Solid-State Battery; Ultra-Thin Battery; High Efficiency CdTe Solar Cell; Solar Energy Harvesting; Thin, Flexible Power Source; Flexible Electronic Power

Introduction

While Li-ion batteries have changed the world we live in, the industry as a whole struggles to meet market demands for ultra-thin, low voltage batteries required for the next generation of flexible electronics, medical devices, wearables, and wireless devices in support of the Internet of Things. While all device manufacturers want more power, current batteries simply have no way to achieve the desired power within the limited space allotted. Within a defined volume, the problem is one of packaging allocation to include: (1) battery (power/energy), (2) hermetic or protective packaging, and (3) battery terminals/connections of the battery to the device.

Figure 1 shows the heart of the challenge, typical lithium ion packaging materials alone are ~200 microns thick. With a large customer base desiring batteries with a total packaged thickness of 100-250 microns, current battery packaging solutions use the entire thickness allotment leaving literally no room for the active battery materials. The emphasis traditionally has been on battery material improvements over novel packaging.

Li-Ion Battery Encapsulation Materials
(Pouch Cell Packaging)

<table>
<thead>
<tr>
<th>Layers from Outside to Inside</th>
<th>Polyamide</th>
<th>Adhesive</th>
<th>Aluminum Foil</th>
<th>Adhesive</th>
<th>Polypropylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness</td>
<td>111 µm (Each Side)</td>
<td></td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Packaging thickness alone ~ 220 µm

Li-Ion Batteries Use Packaging that Limits Their Attainable Energy Density in a Thin, Flexible Package

The advantage of solid state batteries, and thin film solid state batteries in particular, is that there are no liquids to contain and, therefore, the substrate itself can become an integral part of the hermetic packaging without adding significant volume. As a result, solid state batteries can achieve substantially higher energy density. Further, without the traditional pouch cell packaging, the thin film battery format maintains the same energy density from a few substrates to several substrates thick. Therefore, solid state batteries can provide thin, flexible power solutions with capacity ranging from <10 mAh to > 1,000 mAh.

Ultra-Thin Solid State Battery

In a project sponsored by the FlexTech Alliance, ITN and ENrG demonstrated the feasibility of producing high energy density solid state lithium batteries (SSLB) on ultra-thin flexible ceramic substrates (YSZ). Taking advantage of the impervious nature of the YSZ, a battery is produced by vertically stacking SSLB cells deposited on YSZ substrate with an edge sealing adhesive between layers to help protect the battery materials from moisture and oxygen. Figure 2 shows that, without the need for additional packaging, the resultant SSLB battery can be extraordinarily thin, i.e. less than 100 µm total packaged thickness. To enhance the overall energy density, over 80% of the YSZ area is coated with active battery materials.
Figure 2. SSLB packaging employs YSZ as both the substrate and hermetic packaging and edge sealing adhesives between layers (top). SSLB with thickness <100 μm shows stable cycling in high humidity.

Figure 2 also shows SSLB employing this packaging scheme are able to cycle in high humidity with only minimal capacity fade. Similarly, SSLB initially powering devices in ambient conditions, without substantial loss of capacity for greater than eight months. Based on these tests, as well as measured water vapor transport measurements for the packaging materials and accelerated high temperature and high humidity tests, the SSLB packaging is projected to have over five year shelf life with less than one percent capacity loss.

In addition to the novel packaging, ITN and ENrG have recently deposited SSLB on YSZ substrates with a thickness of 20 microns. In some cases, the SSLB thickness is almost as thick as the substrate, leading to very high energy density. Further, the SSLB can be deposited over a range of areas and cathode thickness, all using the same materials and processes. SSLB capacity scales linearly with area and cathode thickness. Figure 3 shows SSLB cells provide very attractive single cell capacities from 1-60 mAh for cells that vary in area from 5 cm² to 100 cm².

Further, Figure 4 shows the SSLB capacity is preserved as the layers are stacked. In this case, two roughly 4 mAh cells are connected in parallel to achieve a battery with 8 mAh capacity. Similar results have been achieved with up to 7 SSLB cells and with individual cell capacities up to 50 mAh. The resultant SSLB battery capacities range from 1 to 340 mAh. Consequently, a scalable range of SSLB can be provided unique to each customer’s needs while maintaining standard materials and processes. Only the geometry, i.e. cell area, number of cells, etc., need modification to achieve the custom SSLB designs tailored to each application end use requirements.

Figure 3. SSLB cells, deposited on 20 μm thick YSZ, have capacity that increases linearly with area and cathode thickness; inset is a large area SSLB.

Given the heightened concerns with lithium based batteries, most recently highlighted by the Samsung Galaxy fires, we confirmed the solid state nature of the SSLB avoids fires and other safety concerns with competing lithium batteries. Up to 20 mAh SSLB have passed critical safety tests such as UL1642 short circuit and crush tests with only modest heating (45°C) and no fires.

Another key advantage of the SSLB is its ability to support high power pulsing. Figure 5 shows SSLB can support prolonged high current pulses while maintaining a battery voltage greater than 3.5 V that is required for many commercial electronics. With rates as high as 10C at the beginning of life and averaging ~6C over the entire discharge range, the SSLB easily powers a range of devices from wireless sensors with RF telemetry to flexible displays and smart watches.
Figure 5. The low SSLB internal resistance supports repeated high current pulses over the entire discharge; in this case 40 mA pulses (10C) at the beginning of life and ~25 mA on average (6C).

Specific to the needs of the defense community, ITn and ENrG worked with the FlexTech Alliance to evaluate the potential benefits of the ultra-thin SSLB technology for powering flexible electronics. As a test case, we identified a flexible electronic print device (FEP) that requires sustained high current pulsing over long durations. Figure 6 shows the SSLB performance relative to a baseline commercial-off-the-shelf (COTS) lithium battery.

A 20 mAh SSLB was able to power the FEP for almost twice as long as was achieved with a COTS battery that also has more than eight times larger volume. Further, a range of SSLB was able to power the FEP for durations that vary linearly with the battery size. Thus, this particular customer now has new options to operate the FEP with a dramatically smaller battery, for significantly longer times in a similar footprint, or some combination of both. Similar benefits are expected for a range of defense and commercial applications.

Figure 6. SSLB achieved over twice the duration with less than one-fourth the size of baseline batteries in powering a flexible electronic device test case chosen in concert with the FlexTech Alliance.

Other promising features of the new SSLB technology are:

- Rapid Charging, i.e. Charging to 75% of full capacity in ~20 minutes,
- Micro-SSLB cells with area as small as 1 mm² with Photolithographic Patterning, and
- Flexible power sources; SSLB with Bend Radius as small as 10 mm have been demonstrated


Recently, the SSLB has been combined with Lucintech’s high efficiency CdTe solar cells to provide in-field recharging. The new product, called a Flexible Integrated Power Pack (FIPP), integrates the SSLB and CdTe PV in a single, vertically integrated package. CdTe PV was chosen not only for its high efficiency, but also due to its ability to be fabricated in a “superstrate configuration” where the thin film solar cell is deposited on the bottom side of the YSZ sheet. This enables the CdTe to share packaging with the SSLB to maximize the amount of energy generation and storage in a very thin package. Namely, the SSLB essentially serves as the backsheet for PV encapsulation eliminating the need for additional sealing adhesive and YSZ layers.

In a new project sponsored by the FlexTech Alliance, the CdTe has successfully been deposited on ultra-thin YSZ substrates (20 μm thick). Figure 7 shows that efficiencies approaching 7% at full sun (AM1.5) have been achieved with CdTe mini-modules that are 25 mm x 76 mm. These dimensions match those of a 20 mAh SSLB that is two layers thick. As the materials and process are further optimized, we expect to reach efficiencies of 10-15% by the third quarter of 2018. Similar to the SSLB, over 80% of the YSZ substrate is covered with active PV materials.

Another benefit of the thin film CdTe PV is the cells are monolithically integrated from cells into modules using a laser scribing and ink fill process. The number of cells in a mini-module can then be optimized to match the control circuitry requirements that route the PV to charge the battery as well as maintain the SSLB in desired voltage range. Using this approach, module voltages from 1-20V are possible within the package size shown in Figure 8.

Figure 7. Flexible Integrated Power Pack (FIPP) combining the SSLB and high efficiency CdTe PV in a single vertically integrated package.
CdTe Mini-Modules on YSZ Substrate (20 μm)
• Module efficiency 7.1% at 1 sun

Figure 8. CdTe mini-modules on YSZ achieved ~7% efficiency. Based on recent small cells with 11% efficiency, module efficiencies ~20% should be possible with further optimization.

Using this approach, the Team expects an ultra-thin FIPP, 31 mm x 76 mm x 250 μm, will produce ~250 mW and charge a 60 mAh battery in one hour. Figure 9 shows that a control circuit that supports the critical FIPP functions:

• Solar charging of the SSLB
• Maintaining the SSLB in the desired voltage range
• Powering a Load with Either the PV or SSLB

All of this is done with a minimal number of microelectronic circuit elements vertically integrated into the FIPP or integrated with the main system electronics.

Summary
Promising new SSLB and FIPP products have been demonstrated on ultra-thin YSZ substrates. By eliminating the need for extraneous packing to protect these devices from water and oxygen, extraordinary energy densities have been achieved. Current SSLB products are achieving up to 600 Wh/l. Recent demonstrations of SSLB on YSZ as thin as 12 μm, in conjunction with other modest materials and process improvements support a roadmap to SSLB energy density >1,000 Wh/l and >200 Wh/kg.

Even more remarkably, the vertical integration of the CdTe PV and SSLB on YSZ substrates enables energy density >400 Wh/l, including the energy harvesting materials thickness. This is higher than many state of the art ultra-thin batteries alone. Table 1 shows some important properties for both the SSLB and SSLB + PV products.

Table 1. Example properties for a SSLB and SSLP+PV Device on Ultra-Thin YSZ. Both achieve very high energy density.

<table>
<thead>
<tr>
<th></th>
<th>SSLB</th>
<th>SSLB + PV</th>
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<tbody>
<tr>
<td>Substrate Area</td>
<td>31 mm x 76 mm</td>
<td>31 mm x 76 mm</td>
</tr>
<tr>
<td>Capacity</td>
<td>Up to 60 mAh</td>
<td>Up to 215 mW</td>
</tr>
<tr>
<td>Charge Time</td>
<td>~1 hour</td>
<td></td>
</tr>
<tr>
<td>Energy Density</td>
<td>Today</td>
<td>Roadmap</td>
</tr>
<tr>
<td></td>
<td>600 Wh/l</td>
<td>&gt;1,000 Wh/l</td>
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<tr>
<td></td>
<td>&gt;400 Wh/l</td>
<td>(Includes PV)</td>
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References
1. Example of typical Li-Ion Packaging Materials, see http://www.mtixtl.com/AluminumLaminatedFilmForPolymerBatteryCase100mmWx210mmL50pcs.aspx
2. See for example, Phase II SBIR Final Report “Multifunctional Fibers for Energy Storage in Advanced EVA systems,” NASA contract number NNJ07JA13C.
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2 See for example, Phase II SBIR Final Report “Multifunctional Fibers for Energy Storage in Advanced EVA systems,” NASA contract number NNJ07JA13C.