Solid-state Thin Film Batteries in 3D

J.R. Gaines, Jr.,
Technical Director of Education
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Solid-state Thin Film Batteries

• How a thin film battery works
• Some examples in 2D
• Some history on the current technology
• New Processes
• New Architectures
**Fig. 2.** Schematic illustration of a thin film battery. The arrows indicate the discharge reaction where a Li ion diffuses from the lithium metal anode to fill a vacancy in an intercalation compound that serves as the cathode. The compensating electron is conducted through the device.
"Thin" means battery @ 20 microns but the substrate is 170 microns!!
• **Unique Technical Features**
  * ‘Perpetually’ rechargeable +75,000 cycles demonstrated by ORNL and Manufacturers*
  * Operating temp range -40 to +200 C*
  * Nominal 4 volts (next gen 5 volts?)*
  * Self discharge <1% per year (studied over 6 years – rates nearly unmeasurable)*
  * Fast recharge to 90% in less than 10 min*
  * Highly embeddable and safe
• Thin AND flexible (Kapton, SS, thin silicon)

Front Edge Technology’s Flexible TFB in action
Lithium ion Vs Electrons

• Size of a Lithium Ion = 182 pico meters

• Size of an electron = 0.00281 pico meters

• A Lithium Ion is nominally 65,000 x larger than an electron – so the anode doubles!!
Battery doubles or triples in thickness on charging
Figure 1: Typical Discharge Curves @25°C (200 μAh Standard Grade Cell)
• Development and Commercialization of Thin Film Batteries
  
  • ORNL developed the technology and nucleated the commercialization process

  • Companies formed specifically to manufacture and commercialize TFB

  • Existing companies have added TFB manufacturing and commercialization to their product line
TFB Manufacturing Process

- Deposit metal electrode on substrate (DC sputter)
- Deposit cathode, LiCoO2 (DC sputter)
- **Break vacuum and anneal**
- Deposit electrolyte, Li3PO4 (Rf sputter)
- Deposit anode layer, Li or other, (evaporation)
- Deposit top metal electrode (DC sputter)
- Encapsulate the battery
- Dice the substrate
Creating Ions to Ablate the Target

DC plasma sputtering

- Substrate/Anode
  - to be coated in cathode material
- Target/Cathode
  - containing raw material that is sputtered off by the positive ions impacts

Background gas
Neutral target atom
Electron
Ionized atom
Negative Glow Plasma
Cathode dark space (CDS)
• Thin Film cathode of LiCoO2 has microstructure that is oriented and dense
Unique Electrolyte that is VERY THIN and pore-free to promote ion transport.

**SEM images: LiPON Thin Film by Nitrogen Reactive Sputtering**

*World No.1 in Thin Film Battery*

Glass-like morphology with smooth surface.
Why is there a market for *Solid-State* Thin Film Batteries?

- The perpetually shrinking wireless gizmo
- Limits on the ‘shrink-ability’ of conventional energy storage technologies
  - Safety concerns with flammable (liquid) electrolytes
- ‘Green Battery’ where device life < battery life
Range of Mobile Devices

• “Big Energy Users” = Mobile Cellular phones

• “Small Energy Users” = Active RFID tags, or IoT, Real time clocks
ST Micro’s ‘EnFilm’ – available for sale now

EnFilm™ - rechargeable solid state lithium thin film battery

Features
- All solid-state
- Ultra thin
- Fast recharge
- Long cycle life
- RoHS compliant
- UL file number: MH47669

Applications
Device is intended to be used in following applications:
- Sensors and sensor networks
- Smart card
- RFID tags
- Energy storage for energy harvesting devices
- Non-implantable medical applications
- Backup power

Table 1. Device summary

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
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<tbody>
<tr>
<td>Capacity</td>
<td>0.7 mAh</td>
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<tr>
<td>Vnominal</td>
<td>3.9 V</td>
</tr>
<tr>
<td>Vop</td>
<td>3.6 to 4.2 V</td>
</tr>
<tr>
<td>Rref</td>
<td>100 ohm</td>
</tr>
<tr>
<td>I</td>
<td>10 mA</td>
</tr>
<tr>
<td>Dimension</td>
<td>25.4 x 25.4 mm</td>
</tr>
<tr>
<td>Thickness</td>
<td>200 μm</td>
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</table>
iPhone 7 Battery Specs

- 1960 mAh capacity
  - Operating draw of 200 mAh
  - About 8 hours of talk time
Planar TFB for Smart Phones?

- ST Micro’s battery at 1 x 1” = 700 microAh

- Will need about 2,800 sqin of TFB to replace existing technology (53 x 53”)

- Tough to fit into a 5 x 2.5” package!
MEM’s based generator for re-charge

MicroGen Systems uses vibration, coupled with Cymbet EnerChip Thin Film Battery
IOT & Wearable Device Positioning & Cymbet Solutions

Enabling Technology for a Better World
• Near term applications include
  • Real-Time Clocks for PC’s, Tablets, Laptops
  • Wireless sensors
  • CMOS back-up
  • SRAM back-up
  • ‘Energy Harvesting’ systems
  • Smart Card
  • Active RFID tags
  • Therapy delivery systems
  • Internet of Things, smart clothing, wearables
SIZE of Real-Time Clocks

EnerChip RTC is Superior to Legacy Coin Cell

Traditional RTC with Battery
Design Approach

EnerChip RTC
with Optimized Crystal

95% Smaller Surface Area!

80% Lower Profile!

<table>
<thead>
<tr>
<th>Type</th>
<th>Length</th>
<th>Width</th>
<th>Square mm Area</th>
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<td>RTC with CR2032</td>
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<td>28.0</td>
<td>896</td>
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<tr>
<td>EnerChip RTC</td>
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<table>
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<tr>
<th>Type</th>
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<tr>
<td>RTC with CR2032</td>
<td>7.0</td>
</tr>
<tr>
<td>EnerChip RTC</td>
<td>1.4</td>
</tr>
</tbody>
</table>
An Industry develops to make Thin Film Batteries

• For the original ‘Bates’ battery:
  • ST Micro (France) enters
  • AMAT builds tools to manufacture TFB’s
  • Apple may have eaten IPS
  • Cymbet on life support
  • ITN Energy Systems on hiatus
  • Schmidt slows
  • GS Nanotech slows
  • Johnson Research, Front Edge
The Internet Of Everything

BI INTELLIGENCE

Connected Cars
Wearables
Connected TVs
Internet Of Things
Tablets
Smartphones
PCs

Number Of Devices In Use Globally (In Thousands)

Source: BI Intelligence Estimates
What’s Next for Thin Film Batteries?

- Commercialization of the ‘Bates’ battery has shown that a battery can be
  - Perfect
  - Permanent

These attributes must be scaled for more capacity
• The Bad News:

No Moore’s Law For Batteries

(electrons are tiny, Li – ions are 16,000 time larger!)
Next Generation Strategies

• Alternative materials coupling
  • Some examples
  • Ongoing search

• New architectures and substrates

• Ongoing exploration of novel deposition techniques
Alternative Cathode Materials

![Diagram showing normalized capacity and coulombic efficiency over cycle number for different materials including LiNi_{0.5}Mn_{1.5}O_{4}, LiPON, and Li. The diagram highlights the performance characteristics of these cathode materials in terms of their normalized capacity and coulombic efficiency.]
Morphology and Thickness

(a) LiCoO$_2$ 0.32 $\mu$m $\times 15,000$

(b) LiCoO$_2$ 2.2 $\mu$m $\times 5,000$

(c) LiCoO$_2$ 6.7 $\mu$m $\times 5,000$

Kurt J. Lesker Company
Enabling Technology for a Better World
Diffusion Lengths for Lithium Ions

- Limits of a few microns, at low discharge rates?
- Arbitrarily thick cathodes subject to extreme stresses, defects, misorientation, etc.
- Much of the Cathode is Along for the Ride
‘Thick Cathode’ Capacity Far from Theoretical

About 81% of theoretical

About 52% of theoretical

(a) LiCoO$_2$ 0.32 µm

(c) LiCoO$_2$ 6.7 µm
Two-sided architecture

Extended architecture
Increase surface area for interfaces (Sakti3)
Advanced Gate Structure

ALD Gate Metal Barrier
Metal Source:
1. TiCl4
2. TDMAT

ALD Gate Oxide
HfO2 Source:
1. TMAH
2. HCl
3. L3 (ARMD)3

元件外接電容 (Capacitor)
ALD ZrO2 或 Al2O3 Source:
1. TEMAH-Zr
2. ZrCl4
3. TMA
4. C12H22N5Zr

Metal Gate
Silicon Substrate
SiGe
ALD - Sequential, Self-Saturating, Process

Legend:
- Precursor A
- Precursor B
- Reaction By-Product
- Inert Carrier Gas
Engineered Gas Flows

- Inactive Gas Flow Distribution Focuses Precursor Onto Substrate Surface During Precursor Pulse Steps*
- Helps Protect Ports and Chamber Walls From Unwanted Precursor Exposure
- PFT™ Enables Efficient Precursor Utilization, Purging, & Eliminates Need for Particulate-Generating Gate Valves

*KJLC Precursor Focusing Technology™ (PFT™) – Patent Pending*
Highly Conformal, Deep trench, AR = 30:1
Atomic Layer Deposition of Electrolytes (two stage process)

Figure 1. Cross-section SEM pictures of the ALD deposited lithium phosphate thin films on Si(100) substrates at (a) 250 °C (LPO250), (b) 275 °C (LPO275), (c) 300 °C (LPO300), and (d) 325 °C (LPO325), after 2000 ALD cycles.
Batteries “More-than-Moore”

- encapsulation
- top electrode
- electrolyte
- bottom electrode
- Si substrate

Current collectors (with barrier layers)
Planar Vs 3D Architecture Structures

- Planar Thin Film Solid State Battery
  - Increase Electrode Thickness
  - Conformal Fabrication in 3D Structure

- Cell Footprint = \( A \)
- Internal Interface Area = \( A \)
- Energy \( \uparrow \)
- Power \( \downarrow \)

- Cell Footprint = \( A \)
- Internal Interface Area > \( A \)
- Energy \( \uparrow \)
- Power \( \uparrow \)
Ion Milling for Substrate Prep

- a: Silicon Wafer
- b: DRIE Hole Array Etch
- c: ALD Battery Layer Deposition
- d: Cu Hard Mask Evaporation
- e: Ar+ Ion Milling Device Isolation
- f: Battery Testing

Steps:
1. Silicon Wafer
2. DRIE Hole Array Etch
3. Ar+ Ion Milling Device Isolation
4. Battery Testing
5. ALD Battery Layer Deposition
6. Cu Hard Mask Evaporation
Pillars Vs Pores – AEF Advantage?
Glancing angle deposition of oriented structures
Lithium anode volume expansion

<table>
<thead>
<tr>
<th>Materials</th>
<th>Li</th>
<th>C</th>
<th>Li₄Ti₅O₁₂</th>
<th>Si</th>
</tr>
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<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.53</td>
<td>2.25</td>
<td>3.5</td>
<td>2.3</td>
</tr>
<tr>
<td>Lithiated phase</td>
<td>Li</td>
<td>LiC₆</td>
<td>Li₇Ti₅O₁₂</td>
<td>Li₄.₄Si</td>
</tr>
<tr>
<td>Theoretical specific capacity (mAh/g)</td>
<td>3862</td>
<td>372</td>
<td>175</td>
<td>4200</td>
</tr>
<tr>
<td>Volume change (%)</td>
<td>100</td>
<td>12</td>
<td>1</td>
<td>420</td>
</tr>
<tr>
<td>Potential versus Li (V)</td>
<td>0</td>
<td>0.05</td>
<td>1.6</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Area Enhancement Factor (AEF)

- Pillars Vs Pores – still need about 30x to break even with Planar architecture

- Smartphone requires AEF of 400!

- Current demonstrations at AEF = 50
Demonstrated Capacity Scales with AEF
ALD Reaction Temperatures

- ALD is a chemistry driven process
- Based on precursor volatility/reactivity

Most ALD Processes

Reactor Temp

Room T 100°C 150°C 150°C 200°C 250°C 300°C 350°C >400°C

Lower precursor volatility, Slow desorption of precursors

High precursor volatility, lower thermal stability of precursors
Remote Inductively Coupled Plasma (ICP)

- 500 W Ar/O₂ plasma
- Cylindrical quartz plasma tube w/ helical inductive coil geometry
- 13.56 MHz frequency
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Gas/Solid Interactions are Classic

- Physiosorption
- Desorption
- Chemisorption
- Effected by –
  - Incident angle
  - Precursor density
  - ‘energy’ (temp, plasma)
Recombination of Hydrogen

- Plasma cracks about 50% of H₂ into H

- (Atomic) H quickly recombines, over a few cm’s, to become H₂ again

Figure 1. Hydrogen recombination simulation geometry (40mmφ x 130mm). Color is mass fraction of H. Input H₂ flow=2.0 srm, P=1.0 Torr, γ =0.01.
Recombination of Ions in Trenches
Example of Steric Hindrance
Growth per cycle Less than 1 mono layer

- typically ~5-50% of ML
- limited by:
  - steric hindrance?
  - number of reactive sites?
  - other factors?

Less than ML growth has consequences to growth mode and layer characteristics
Random Growth Mode
Modeling of ALD Film Growth

• Add Univ of Alberta data on ALD in deep vias.

• Modification of pulse times to fully occupy all available functionalized sites

• Alternative pulsing patterns to optimize growth-per-cycle
ALD Capping Layers for TFB’s

Water Vapor Transmission Rate (WVTR) $<10^{-6}$ g/m2 day demonstrated
• Other substrates and architectures
Micro-thin substrates Lithium ion conductor - Ohara
Ultra thin glass – 25 microns - Schott Optical
Foam and Aerogel Electrodes
• **Summary**

  • More than 20 years in the making

  • Showed the way toward a perfect, permanent battery and re-energized battery research

  • *Convergence of electronic device design (smaller, more energy efficient) & solid-state secondary microbatteries = commercialization*
KURT J. LESKER COMPANY

J.R. Gaines, Technical Director of Education
JRG@Lesker.com
614-446-2202