

# Energy Storage in Thin Sputtered Films

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# J.R. Gaines Bio

- Career in advanced materials development, manufacturing and commercialization
  - Temperature sensors
  - High Tc Superconductors
  - Ceramic powders, sputter targets
  - Thin Film Batteries













# Thin Film Batteries What is a thin film battery?

- How is a thin film battery made?
- How does it compare to conventional batteries?
- What are it's commercial applications?
- What is KJLC's position in this market?





- 'THIN' means the active thin film layered stack is 15 – 20 microns thick
- (+thickness of the substrate/host ~ 170 microns)



# How a TFB works (Dudney, ORNL)



**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.





 Unique microstructure that is oriented and dense



Lithium cobalt oxide after high temp anneal



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Unique Electrolyte that is VERY THIN and pore-free to promote transport

SEM images : LiPON Thin Film by Nitrogen Reactive Sputtering

World No.1 in Thin Film Battery



Glass-like morphology with smooth surface.



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Figure 1: Typical Discharge Curves @25°C (200 µAh Standard Grade Cell)





### Thin AND flexible (Kapton, SS, thin silicon)



Front Edge Technology's Flexible TFB in action

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- Unique Technical Features
  - 'Perpetually' rechargeable +75,000 cycles
     demonstrated by ORNL and Manufacturers
  - Operating temp range -40 to +200 C
  - Self discharge <1% per year (studied over 6 years)</li>
  - Fast recharge to 90% in less than 10 min
  - Highly embeddable and safe



# **TFB Manufacturing Process**



 Deposit metal electrode on substrate (DC sputter)
 Deposit cathode LiCoO2 (DC

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



# **TFB Integration with Host**

#### EnerChip Silicon Wafer







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 electrolytes
- 'Green Battery' where device life = battery life
- The 'permanent' battery Kurt J. Lesk



- Near term applications include
  - Wireless sensors
  - CMOS back-up
  - SRAM back-up
  - 'Energy Harvesting' systems
  - Smart Card
  - Active RFID tags
  - Therapy delivery systems



# **Commercial Products (IPS)**



Actual size 1 x 1 x 0.007"

Capacity 1 micro Amp Hour



Figure 2: Typical Discharge Curves @25°C (0.7 mAh Performance Grade Cell)



### ST Micro's 'EnFilm' $\overline{\mathbf{A}}$

#### EFL700A39

EnFilm<sup>™</sup> - rechargeable solid state lithium thin film battery

#### Datasheet - preliminary data

**ExFilm** 

EFL700A39

N04Au00

#### 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
- RF ID tags
- Energy storage for energy harvesting devices
- Non implantable medical applications
- Backup power

#### Description

The EFL700A39 is a thin film rechargeable lithium battery. The battery has a LiCoO2 cathode, LiPON ceramic electrolyte and a lithium anode. This device has a footprint of 25.4 x 25.4 mm.

#### Table 1. Device summary

Symbol	Value
Capacity	0.7 mAh
Vnominal	3.9 V
Vap	3.6 to 4.2 V
Ret	100 ohm
<del>ه</del>	10 mA
Dimension	25.4 x 25.4 mm
Thickness	200 µm





### Cymbet/Texas Instruments Energy Harvesting Platform



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## **Demonstration Platforms**

#### **CBC-EVAL-06 EnerChip CC RTC Evaluation Kit**

**CBC-EVAL-06 Module Connector, Jumpers, and Test Points** 





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# Infinite Power Solutions Applications Development Kit



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#### **Two-sided architecture**

### **Conformal feature of TFB's**



#### **Experimental TFB on fiber**



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# **Next Generation Applications**

- Smart Phones
- Tablet computers
- Laptops
- Solar panels
- Smart clothing





# **Coin Cell Performance**

#### ENERGIZER CR2430



#### **Typical Discharge Characteristics**

Load: 10K ohms - Continuous Typical Drain @ 2.9V: 0.29 mA



Capacity 290 mAh



0.10 (0.004) Minimum Ref. (Applies to top edge of gasket or edge of crimp, whichever is higher.)

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### Other 'thin' batteries

### – Printed Batteries



**Power Paper 1.5v Primary Battery** 

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### Performance of TFB Vs Printed Batteries

Power Paper STD-3 Premium (primary battery) *IPS THINERGY MEC101* (secondary battery)

Outline Dimensions 39 x 39 mm

Nominal voltage 1.5v

Nominal Continuous

Current 0.5 mA

Nominal Capacity 30mAh

Shelf life

3 years

25 x 25 mm

3.9v

40mA

1mAh

10 years

Self Discharge Rate 20% p/year

1% p/year

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- 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





#### Early publications attracted commercial interests:

- J. B. Bates, G. R. Gruzalski, N. J. Dudney, C. F. Luck, and X. Yu, "Rechargeable Thin-Film Lithium Batteries," Solid State Ionics 70/71, 619 (1994).
- J. B. Bates, G. R. Gruzalski, N. J. Dudney, C. F. Luck, and X. Yu, "Rechargeable Thin-Film Lithium Batteries," p. 213 in Proceedings of Eighth Electronic Materials and Processing Congress, ed. by S. T. Rao, ASM International, Materials Park, Ohio, 1994.
- J. B. Bates, G. R. Gruzalski, and C. F. Luck, "Rechargeable Solid State Lithium Microbatteries," p. 82 in Proceedings of IEEE Workshop on Micro Electro Mechanical Systems, The Institute of Electrical and Electronics Engineers, Piscataway, New Jersey, 1993.
- J. B. Bates, N. J. Dudney, C. F. Luck, B. C. Sales, R. A. Zuhr, and J. D. Robertson, "Deposition and Characterization of Li2O-SiO2-P2O5 Thin Films," J. Am. Ceram. Soc. 76, 929 (1993).
- J. B. Bates, G. R. Gruzalski, N. J. Dudney, C. F. Luck, X. Yu, and S. D. Jones, "Rechargeable Thin-Film Lithium Microbatteries," Solid State Technology 36 (7), 59 (July 1993).

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### 'Pure Play's in Thin Film Batteries

- Infinite Power Solutions (Colorado)
- Cymbet (Minnesota)
- Oak Ridge Micro-Energy (Tennessee)
- Planar Energy Devices (Florida)
- GS Nanotech (S. Korea)





- Companies that added TFB
  - Front Edge (California)
  - ITN Energy Systems (Colorado)
  - Excellatron (Georgia)
  - Schmid (Germany)
  - ST Micro (France)
  - Others who can not be named





- Sputter target evolution
  - Refinement of target chemistry to enhance manufacturing
    - Compensation for Li losses in processing
    - Electrical conductivity of LiCoO2 cathode target
    - Phase and chemical purity of Li3PO4 targets

 Growth in target size since 1994's from 2" diameter to 1 sq meter in 15 yrs



# LiCoO<sub>2</sub> & Li<sub>3</sub>PO<sub>4</sub> Powder

- Batch size ~45 kilos
- Dedicated mixing/ milling equipment to avoid crosscontamination



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# Sintering (330mm OD Blank)





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# Machining

- Dedicated grinders
- Diamond tooling
- Dust proof enclosures to prevent cross contamination



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### **Typical Phase Purity of LiCoO<sub>2</sub>**



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## **Typical Phase purity of Li<sub>3</sub>PO<sub>4</sub>**



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# Typical Electrical Resistivity of Sintered LiCoO<sub>2</sub> Targets





KJLC<sup>®</sup> Confidential 2-point Resistance Usi

2-point Resistance Using Metal Contacts

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The ORNL-developed Thin-Film Array Slide

Power Paper's Powered Cosmetic Delivery Patch



Solicore's Powered Smart Card



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- Where is the money Coming from?
  - Applied Materials
  - Bekeart
  - Core-Capital
  - D.E. Shaw Ventures
  - ST Micro

- Intel
- DOW
- In-Q-Tel (CIA)
- Millennia Materials
   Fund
- Texas Instruments





- Design firms qualified for TFB systems integration
  - Advanced Solution Corporation
  - Pacific Design Engineering
  - Synapse Product Development
  - Winland Electronics





Design awards going to TFB manufacturers

- Infinite Power Solutions
  - VDC Research Group's "BEST IN SHOW" at the Embedded Systems Conference
  - IDTechEx's "Best of Sensors Expo" Award
  - INFINERGY™ Micro Power Module (MPM) was the winner of the *IDTechEx Energy Harvesting Award* for Enabling Perpetually Powered Micro-Electronic Devices





### More Kudos

- Cymbet
  - Sensor Magazine's "Best of Sensors Expo 2009" bronze award
  - Frost & Sullivan Recognizes Cymbet for its Innovative Component-Class Thin-film Batteries for Direct Integration into Electronic Devices and SMT Components





- Retail products available through traditional electronic component suppliers such as:
  - Digi-Key
  - Mouser
  - TI e-store











### Summary

- Technology commercialization is a long and brutal process [Bleeding Edge of Technology]
- (20 years and counting for TFB's)
- Match of technical attributes with a market opportunity, some charismatic champions with faith (technical risks/costs), and some patient money that loves risk
- Economic conditions impact the amount of risk loving money available





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