NCCAVS Annual Symposium February 23, 2017

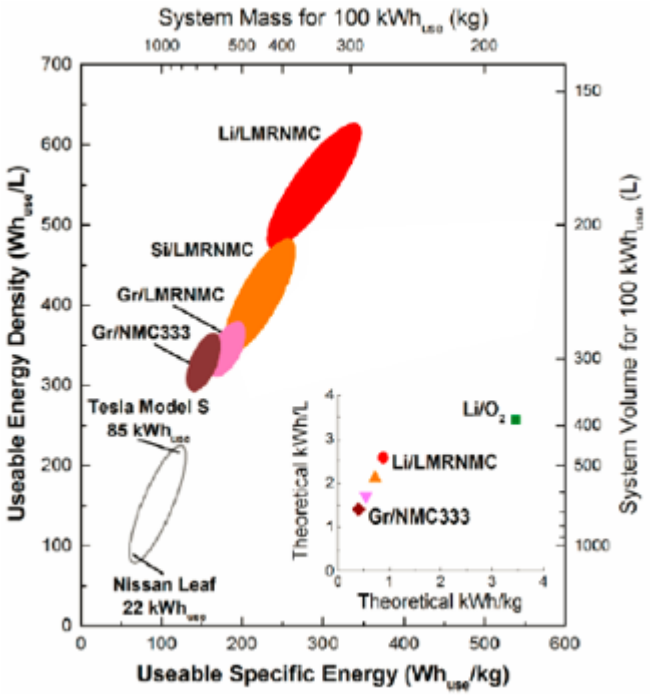
LARGE-SCALE THIN FILM BATTERY

Ernest Demaray (*Demaray LLC*) & Pavel Khokhlov (*SpectraPower LLC*)

- *SpectraPower* High Energy Density Li-metal cells
  - The 6.6Ah battery with proven 480+ Wh/kg, 1500Wh/l
- Thin Film Solid State Electrolyte (SSE) for high cycle life
  - *Antropy Tech/Demaray LLC* defect Free SSE for protection of the anode
- High volume manufacturing - cost and Earth Friendly Material
- Intellectual Property – Integrated thin film high capacity battery
- Performance Projections and First Results
- Feasibility Conclusions
- Comparison with Current Battery Performance and Cost
- Market Application Examples

Hybrid- High Cap NMC and µ-Battery Cell

If Li metal were successful, options open up

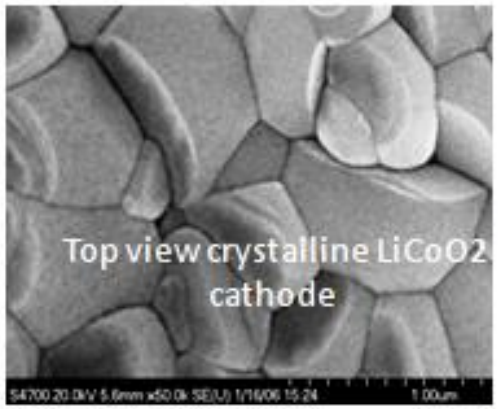


Energy Environ. Sci.,2014, 7, 1555-1563

Cell Performance	SpectraPower anode-less High Cap NMC cell	EnFilm™ thin film µ-battery	hibrid Thin Film high Cap NMC cell
Amp-h	3.2	.7 E^{-3}	3.2
kWh/kg	500	14	500
kWh/L	1500	0.008	1500
Ω	0.144	100	0.144
voltage	3.7	3.9	3.7
fDOD cycle life	20	~80,000	> 5000
self discharge	2%/day	none	none

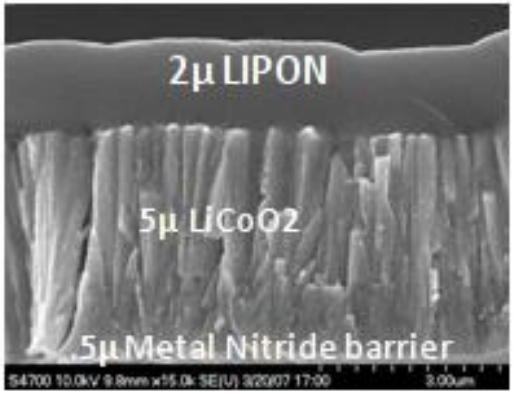
Symmorphix-Demaray LLC
LIPON/LiCoO2 TF-uB

LIPON/LiCoO2 TF-uB sputtered at high rate from a conductive ceramic target with system and license for the Infinite Power Systems (IPS) "Thinergy" battery.

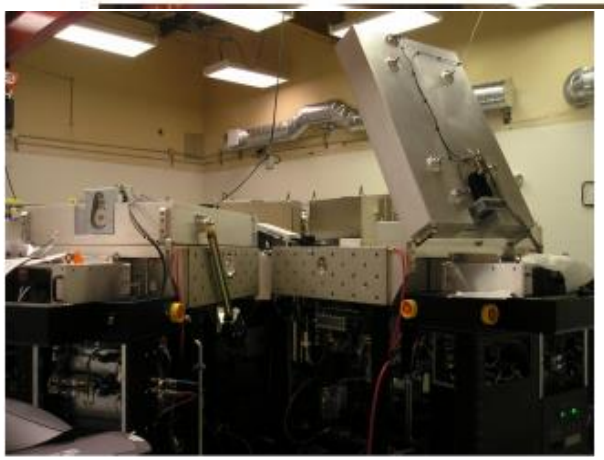


+

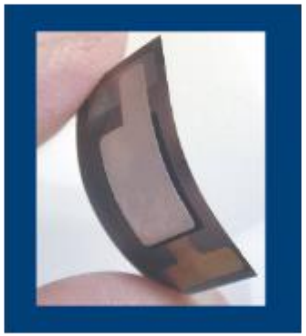
=



H. Zang - E. Demaray designed cluster tool with 5 chambers for sputtering of layers without cross contamination; RF biased Pulsed DC reactive sputtering, first unite for IPS February 2005.



=



,

IPS "Thinergy" TFµB on Cu/Ni foil

DLLC Solid State, Thin Film Battery Intellectual Property

Demaray LLC Core Patents; Biased PDC and RF Sputter Applications

US6,533,907 Method of producing amorphous silicon for hard mask and waveguide applications

US8,105,466 Biased pulse DC reactive sputtering of oxide films

US7,413,998 Biased pulse DC reactive sputtering of oxide films

US7,544,276 Biased pulse DC reactive sputtering of oxide films

US7,381,657 Biased pulse DC reactive sputtering of oxide films

US7,378,356 Biased pulse DC reactive sputtering of oxide films

1. RF biased RF deposition of glassy conformal defect free LIPON

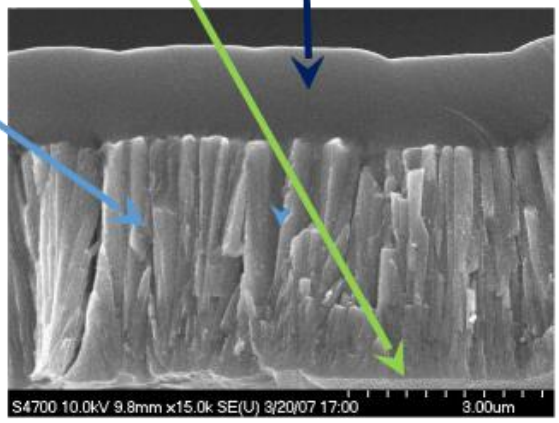
2. reactive BPDC conductive barrier for metal foil

High Rate Deposition of crystalline LiCoO2 cathode

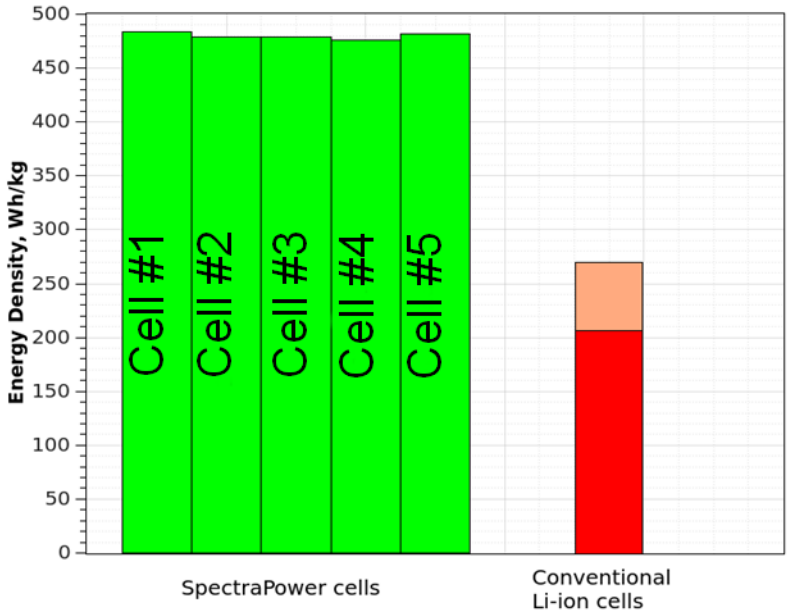
US8,636,876 B2 Deposition of LiCoO2 2014 **3.**

- China ZL200580042305, 2010,
- EU 1825545, 2009,
- Japan 5095412, 2012,
- South Korea 10-1021536, 2011,
- Taiwan 1346403, 2011,
- France 1825545, 2009,
- Germany 6020050175 12.1, 2009,
- Italy 1825545, [illegible]
- China published

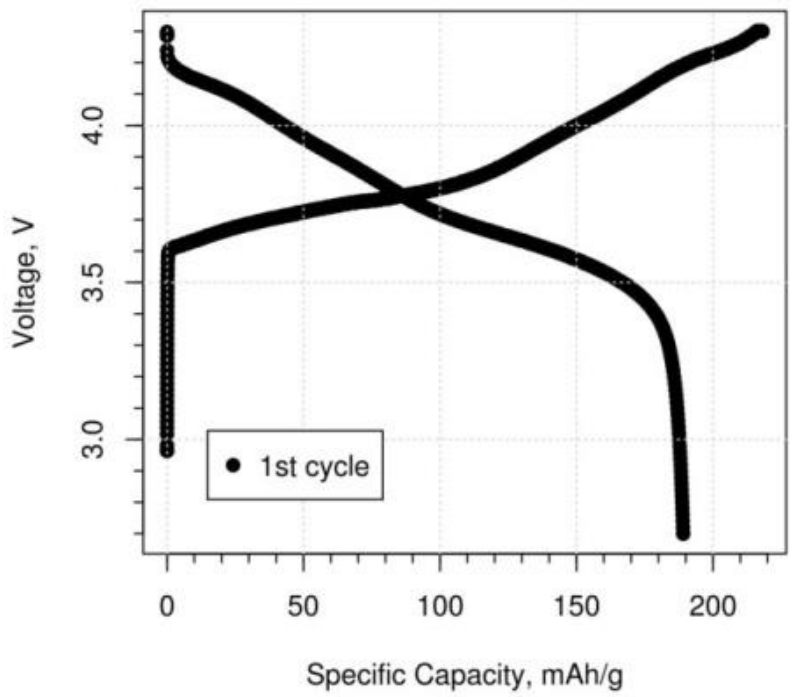
Infinite Power Solutions (IPS) & Apple TFB



Ultra-High Energy Density Rechargeable Li-metal Cells



Ultra-High Energy Density Rechargeable Li-metal Cells

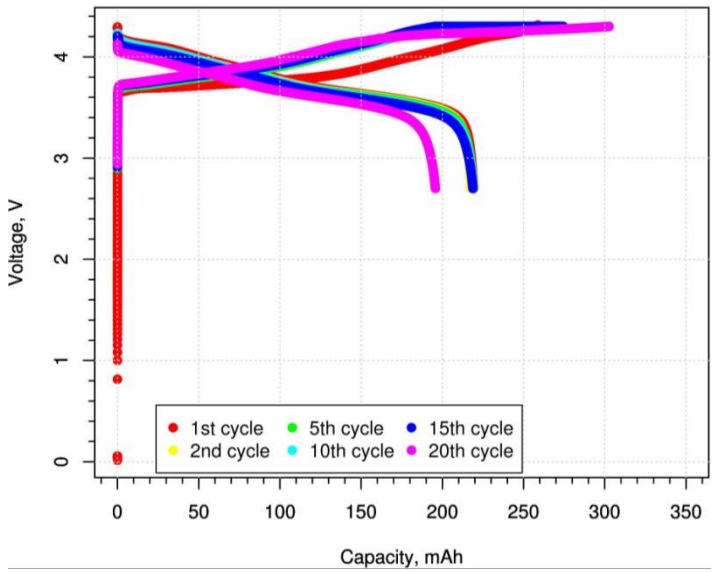


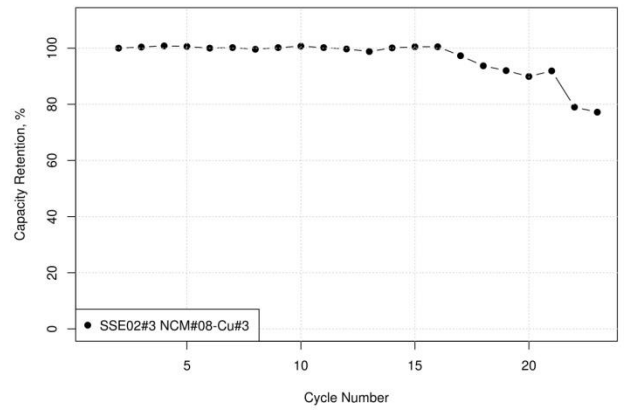
Cycle #	1
Cap., Ah	6.7
Cap., %	100
Cap., mAh/g(cathode)	189.1
Cap., mAh/g(active)	194.9
Cap., mAh/cm2	8.6
Eff., %	86.7
Mid Voltage, V	3.768
Energy, Wh	25.1
Energy, mWh/g(cell)	484.1

Cathode Loading: 45.5 mg/cm2

Cell Weight: 51.8 g

Problem: Limited Cycle Life Performance





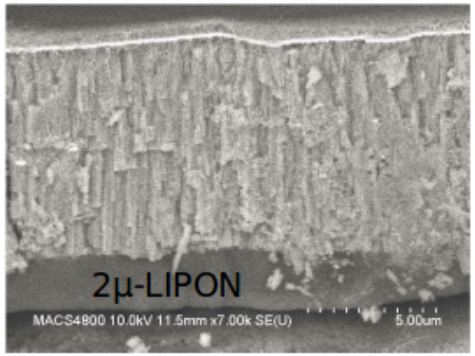
Anode failure as a primarily reason for cell degradation:

- Mossy lithium growth during charge
- Non-uniform Li stripping during discharge
- Copper roughness promotes lithium dendrite nucleation
- No barrier to dendrites growth

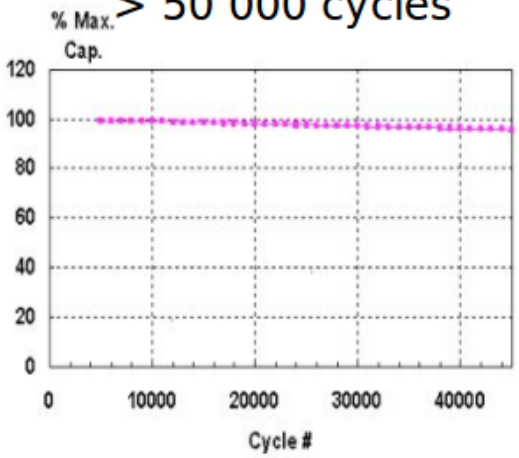
Solution: Micro-Battery Technology

- TF-SSE is proven in manufacturing to efficiently prevent growth of dendritic lithium
- Stable cycling is proven in µ-batteries (~ 1 mAh) in production: all based on LIPON electrolyte as developed by John Bates - ORNL and Oak Ridge Batteries Inc.

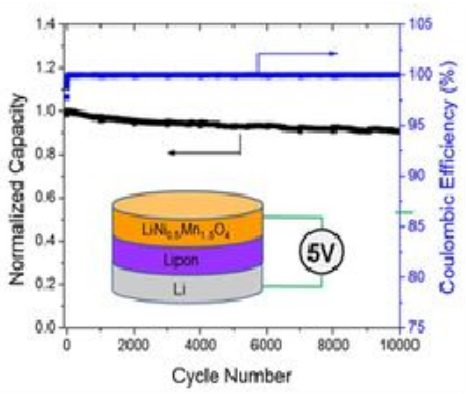
STMicro EnFilm™ Battery
4000 cycles
Warranted by manufacturer



Excellatron data
> 50 000 cycles

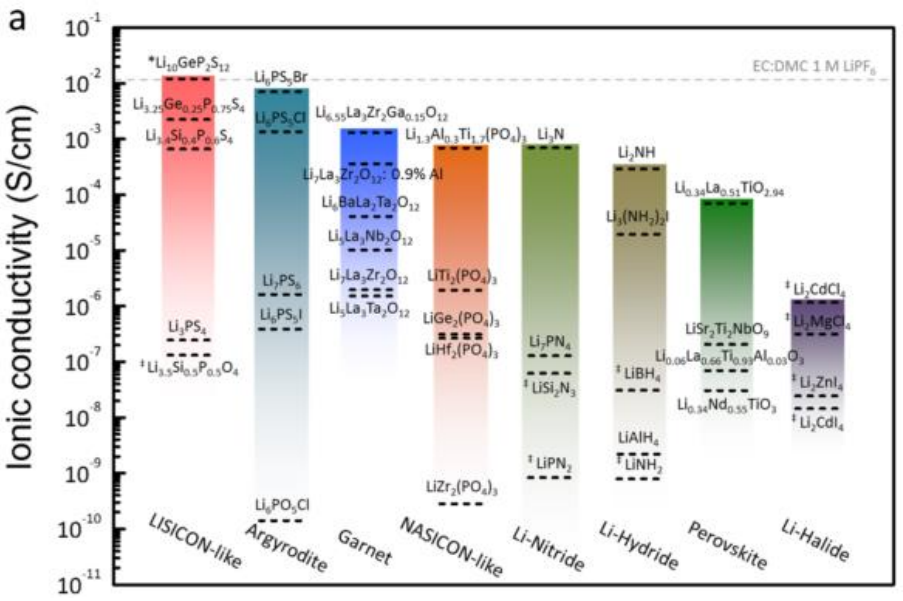


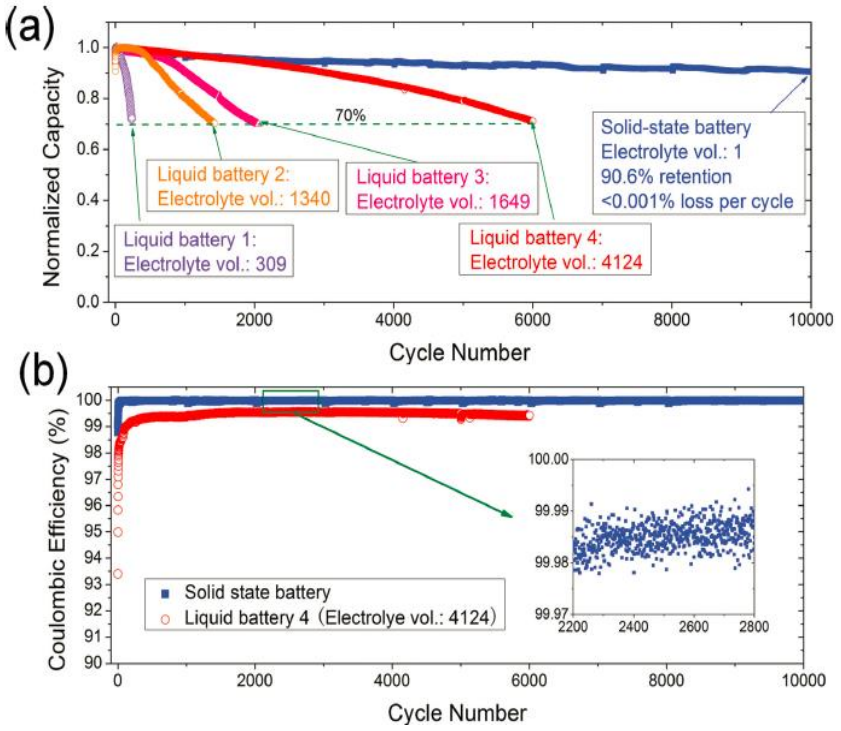
ORNL data – N. Dudney, et. al.
> 10 000 cycles



http://ceramics.org/wp-content/uploads/2011/08/energy-ss-batteries-jones.pdf
Adv. Energy Mater. 2015, 5, 1401408

Solid State Electrolyte



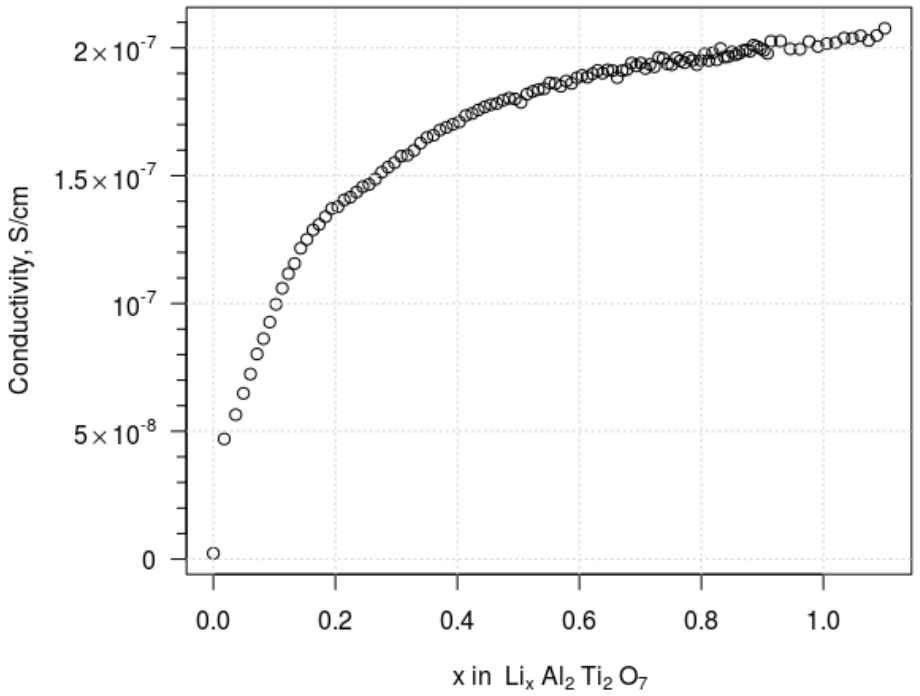


Ionic conductivity of the SSE should be at least $2 \cdot 10^{-5}$ S/cm

J. C. Bachman et al., "Inorganic Solid-State Electrolytes for Lithium Batteries: Mechanisms and Properties Governing Ion Conduction," Chem. Rev., vol. 116, no. 1, pp. 140–162, 2016.

J. Li et al., "Solid Electrolyte: the Key for High-Voltage Lithium Batteries," Adv. Energy Mater., vol. 5, no. 4, p. 1401408, Feb. 2015.

Lithiation From Cathode



Feasibility proof of electrochemical lithiation of the non-conductive oxide layer inside the assembled cell during first formation charge.

SSE of choise: Ga-substituted LLZO: $5.4 \cdot 10^{-4}$ S/cm at 20 °C

$$La_{(54.6a\%)}Ga_{(15a\%)}Zr_{(30.4a\%)} \text{ intermetallic} + 6O_2 = La_{6.55}Ga_{0.15}Zr_2O_{12},$$
$$La_{6.55}Ga_{0.15}Zr_2O_{12} + 7Li = Li_7La_{6.55}Ga_{0.15}Zr_2O_{12} \quad (E = 0V \text{ vs. } Li/Li^+)$$

RF-biased Pulsed DC Sputtering

STMicro **Proven high volume manufacturing – low cost, earth friendly material**

EnFilm™ µ-battery

Features

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

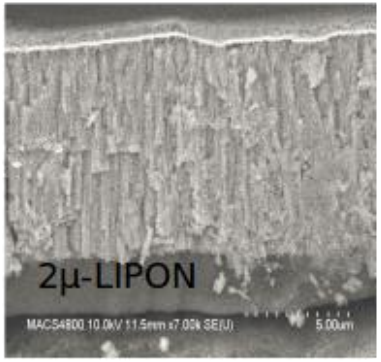
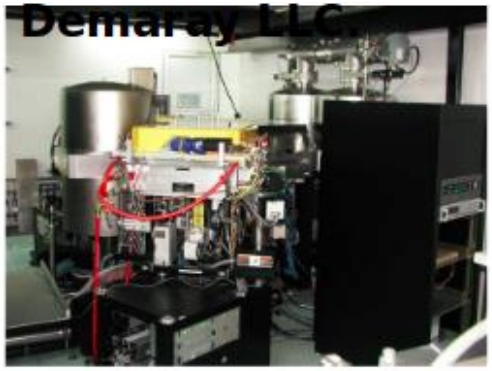
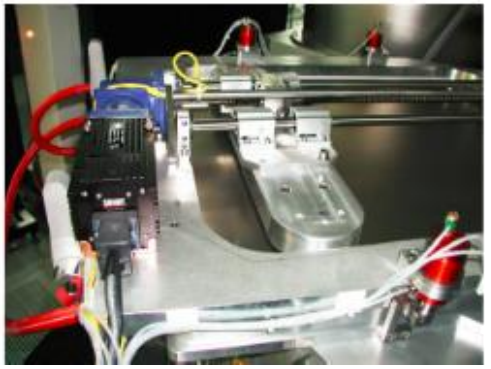


Table 1. Device summary

Symbol	Value
Capacity	0.7 mAh
$V_{nominal}$	3.9 V
V_{op}	3.0 to 4.2 V
R_{int}	100 ohm
I_p	10 mA
Dimension	25.7 x 25.7 mm
Thickness	220 µm

Wide area production scanning magnetron developed and shipped by Symmorphix to STMicro, 2004 with license for Bias Pulsed DC Sputtering Patents now owned by Demaray LLC



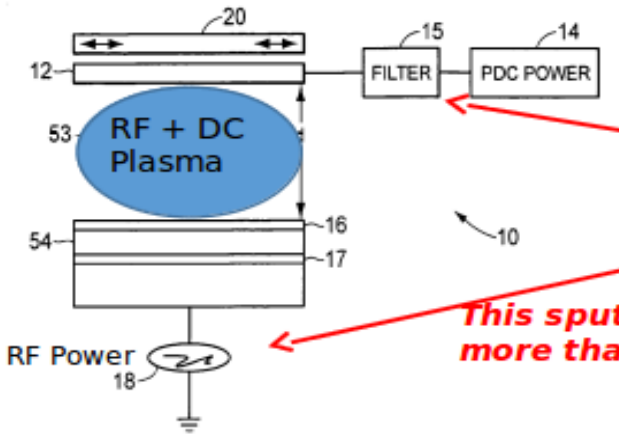


United States Patent

Zhang et al.

(10) Patent No.: US 7,544,276 B2
(45) Date of Patent: Jun. 9, 2009

- "Biased Pulsed DC Reactive Sputtering of Oxides" - the Reactor
- -defect free electrical and optical film production



Reactor Patent has 3 components

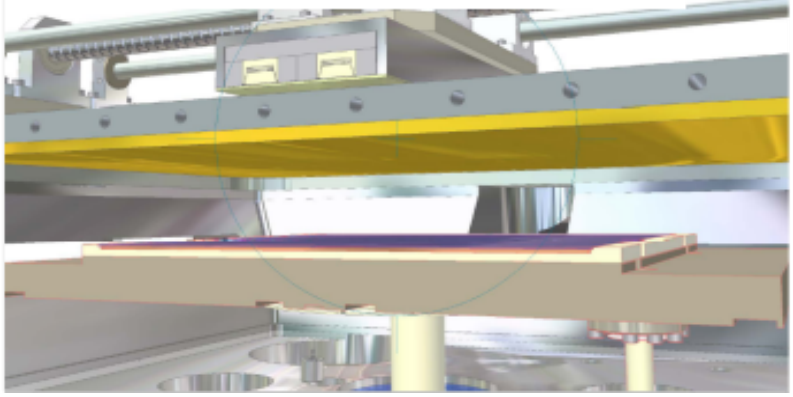
A pulsed DC power supply connected to the sputter target
- more than 5,000 systems have this

A filter to protect the DC supply from the RF supply
– this is required to protect the DC supply

An RF bias power supply connected to the substrate
– far more than half of the systems have this

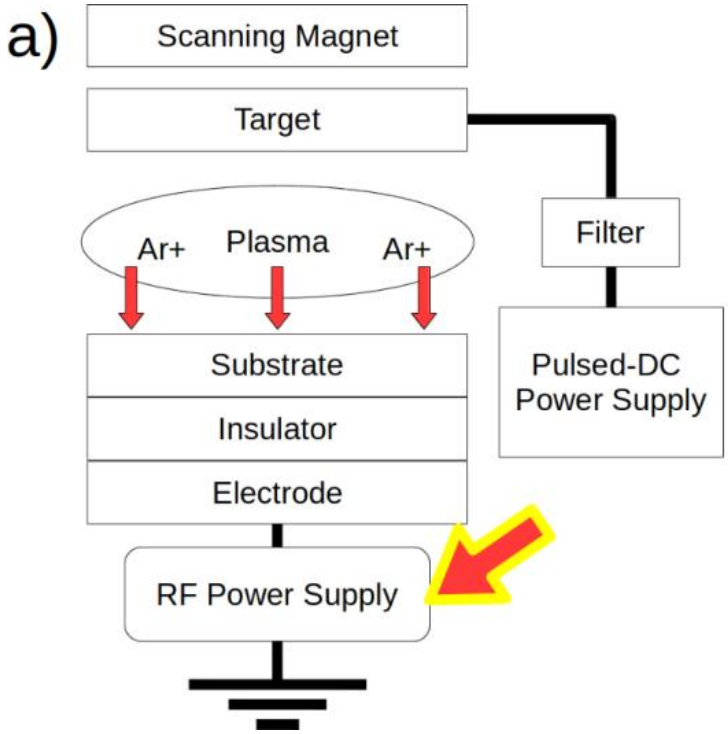
This sputter reactor power configuration is adapted by more than 5000 production sputter systems in production world wide

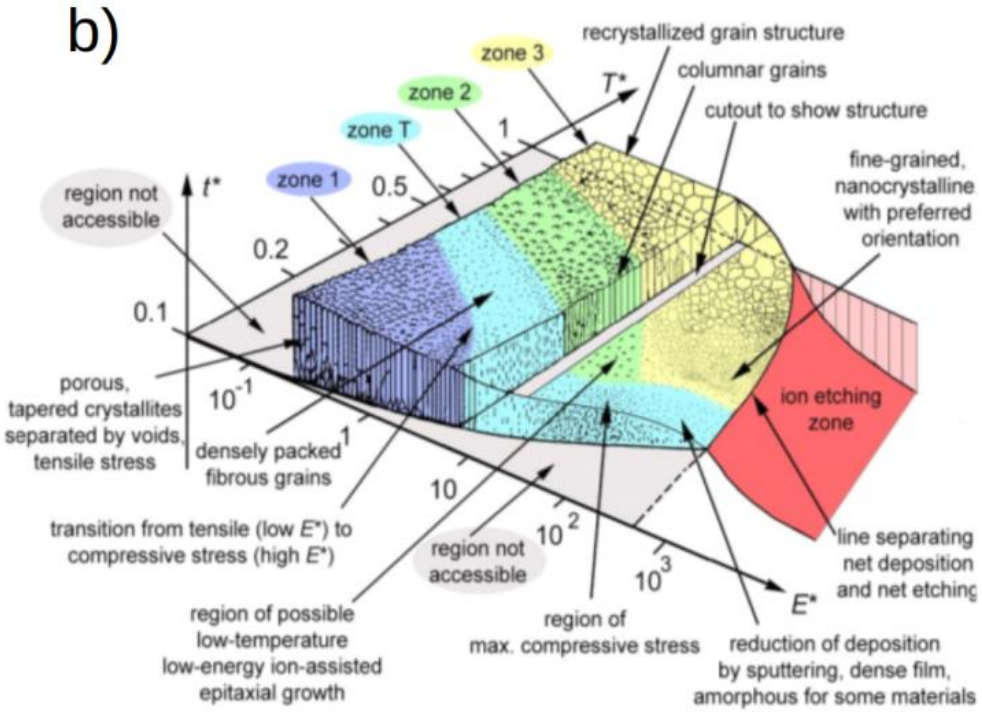
FIG. 1A



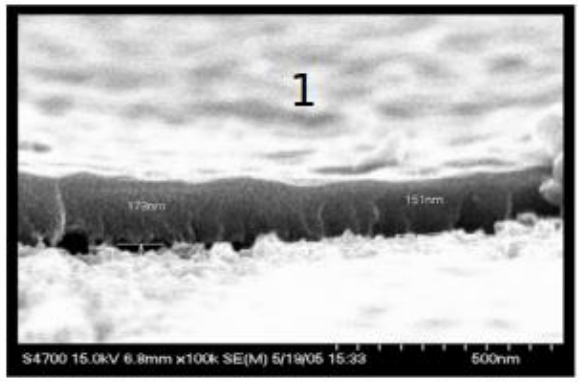
1. A reactor according to the present invention, comprising:
a target area for receiving a target;
a substrate area opposite the target area for receiving a substrate;
a pulsed DC power supply coupled to the target area, the pulsed DC power supply providing alternating negative and positive voltages to the target;
an RF bias power supply coupled to the substrate; and
a narrow band-rejection filter that rejects at a frequency of the RE bias power supply coupled between the pulsed DC power supply and the target area.

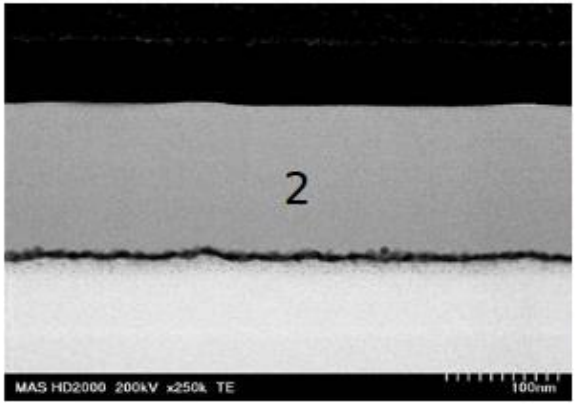
RF-biased Pulsed DC Reactive Sputtering

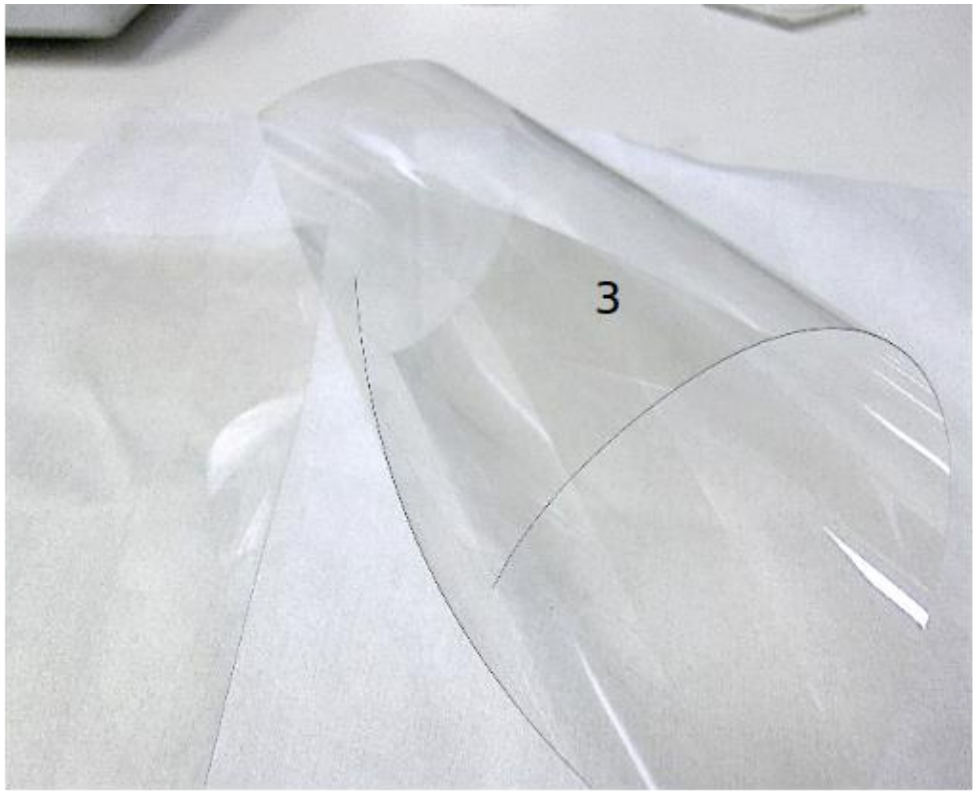




Dielectric barrier film 1 ft2 protecting Indium metal coated PEN – 1 hr. boiling water test.



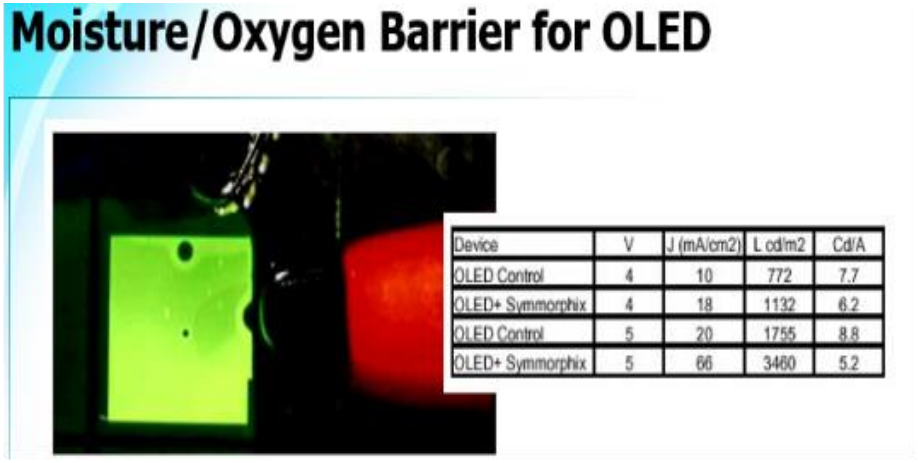




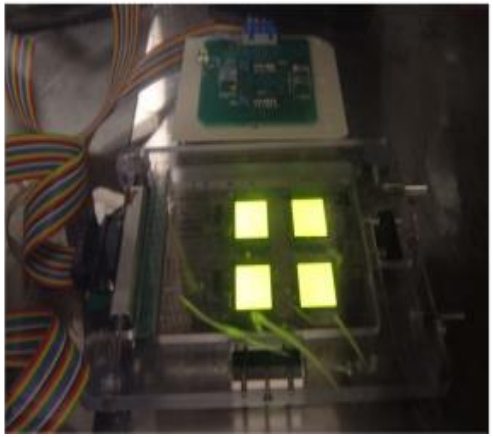
1. SEM fracture cross section of 180nm oxide barrier film over Indium metal on PEN
2. TEM cross section of oxide barrier film over indium on PEN
3. 1Ft square sample of barrier film shown in 1&2 after 1 hr boiling water immersion

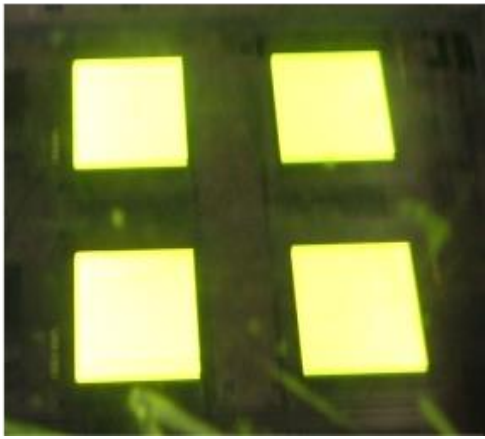
Defect free single layer oxide barrier film protects metallic Ca anode for OLED tested in damp heat

- Ca is more reactive to Oxygen and water vapor than Li metal. Ca is necessary as an electron injection anode layer for OLED light emission.
- Single point defects develop and can be located and sized for water vapor permeation rate as they form a region of oxidation of the Ca that grows in time quantitatively as the thickness of the Ca film is known. The OLED grows dark where the Ca is oxidized.
- Defect free barrier films were first demonstrated by Symmorphix and Dupont under a U.S. Display Consortium grant, 2003-4 by H.Zhang and E. Demaray. Their work independently tested by Dupont resulted in the demonstration of active Ca anode OLED devices surviving 1654 hours in damp heat. This work resulted in the award of a patents claim US7,262,131B2 and US7,205,662,B2, Dielectric Battier Layer, 2007 with allowed claims for a barrier with permeable defect concentration less than ~ 1 per cm^2, including a barrier over a soft metal.

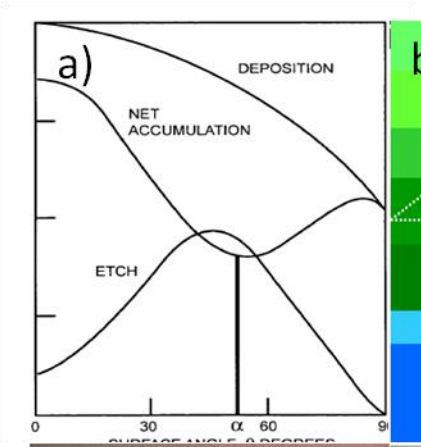


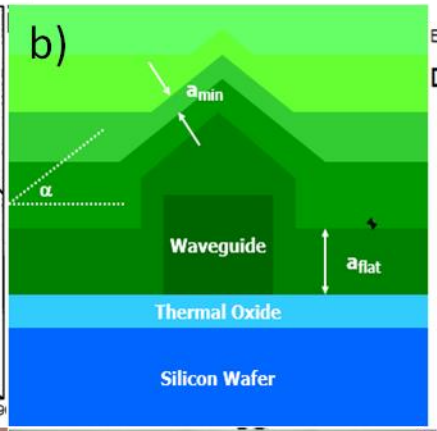
Device	V	J (mA/cm2)	L cd/m2	Cd/A
OLED Control	4	10	772	7.7
OLED+ Symmorphix	4	18	1132	6.2
OLED Control	5	20	1755	8.8
OLED+ Symmorphix	5	66	3460	5.2

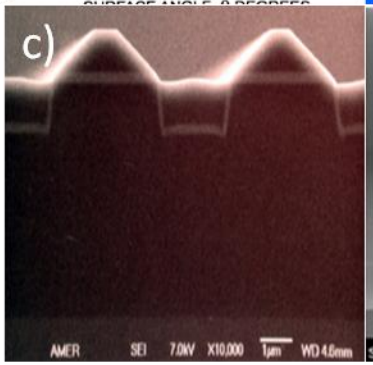


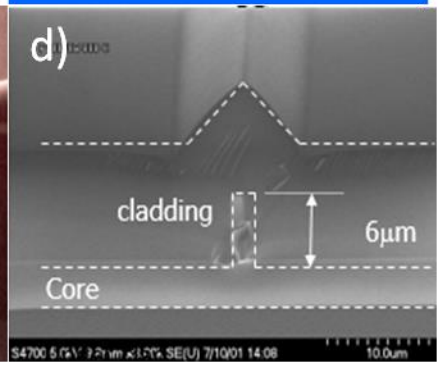


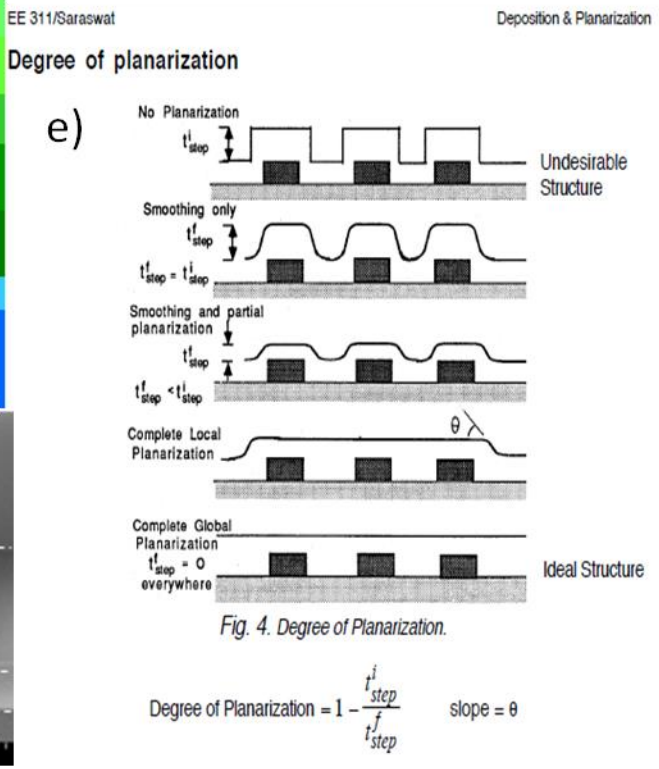
Planarization Layer



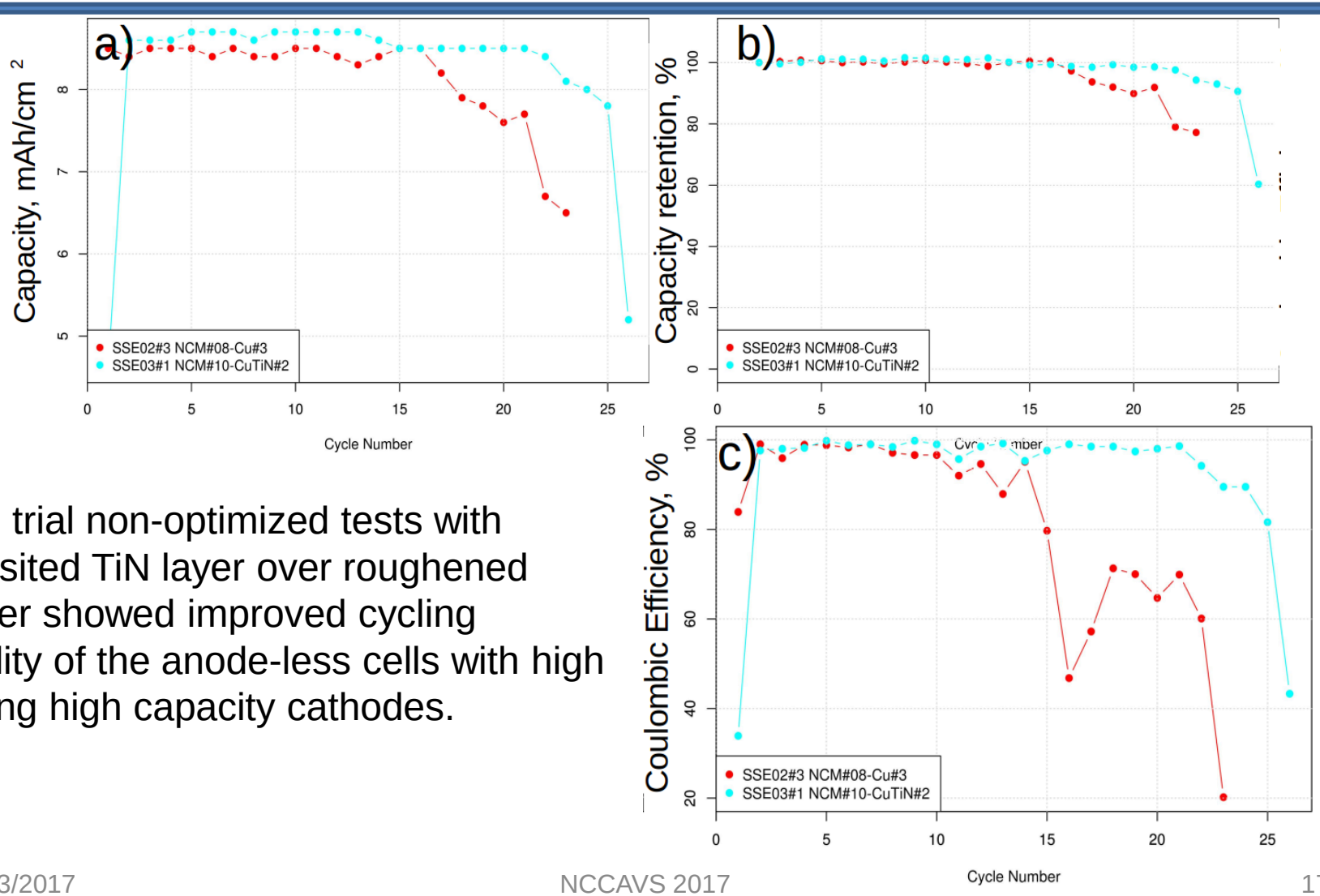






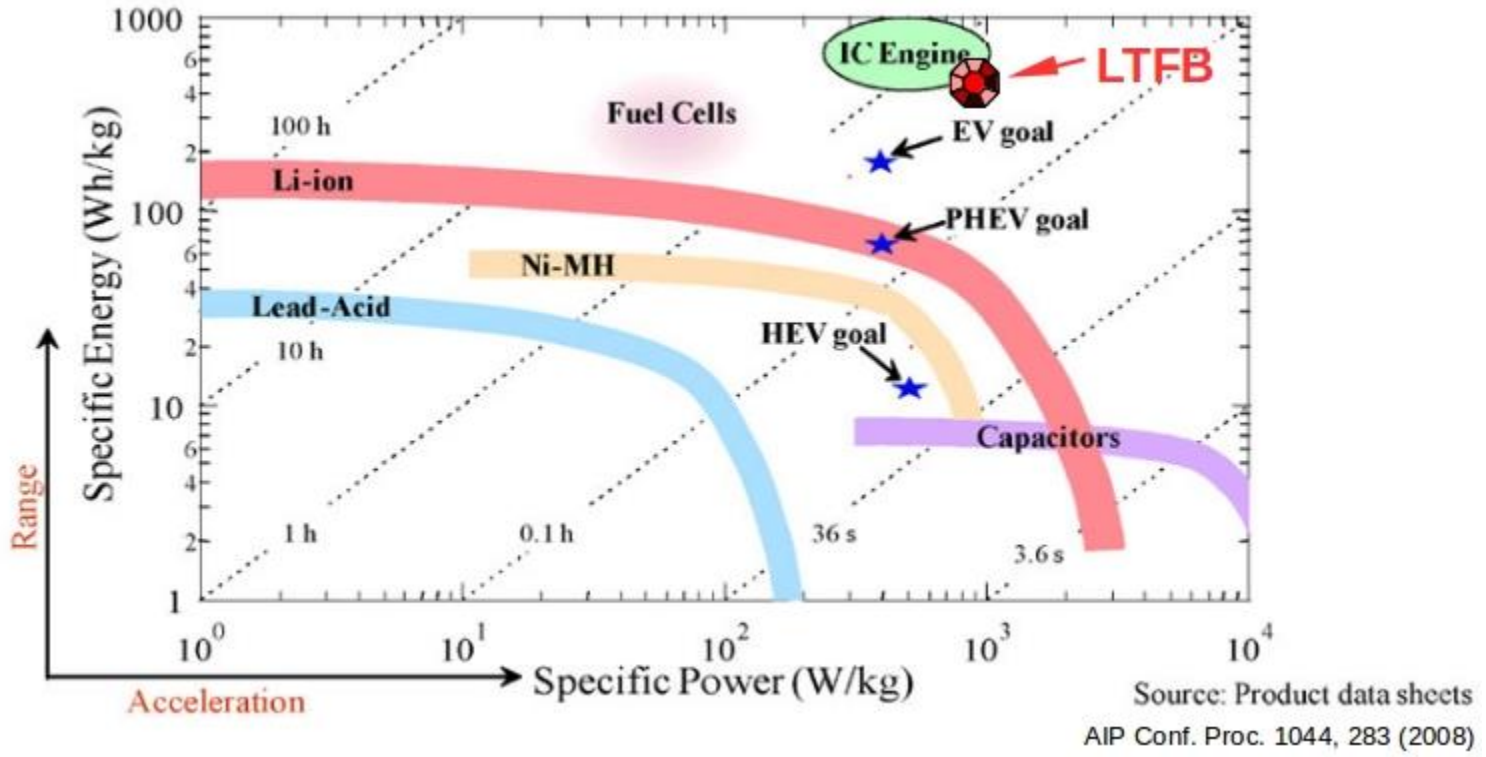


Planarization Improves Cycle Life



Even trial non-optimized tests with deposited TiN layer over roughened copper showed improved cycling stability of the anode-less cells with high loading high capacity cathodes.

Performance Projections



Source: Product data sheets
AIP Conf. Proc. 1044, 283 (2008)

Conclusions

- SpectraPower has demonstrated >480 Wh/kg (cell level) rechargeable “anode-less” battery with capacity 6.6 Ah
- Demaray LLC Thin Film micro battery; production proven to > 10,000-50,000+ cycle with defect free thin film electrolyte and surface planarization for amorphous solid state electrolyte.
- Each technology component has been independently demonstrated. New high conductivity oxide electrolytes are available with Li metal durable and earth abundant solid state oxides and nitrides.
- Integrated process has demonstrated equivalent ~ 500Wh/kg with lithiation of oxide solid state electrolyte and uniform plating of ductile Li metal on the passivated thin film anode.
- Cost; ~ $100/kWh full production opens large scale cost sensitive applications for batteries with service life = > product life.
- Low self discharge and high temperature operation provide safe, secure, on demand power with charging latency of many years.
- ~ 20 allowed Biased Pulsed DC sputtering patents for planarized and amorphous thin films granted for proprietary market franchise and license.
- Provisional Patent; “Thin film Battery with High Capacity, energy Density and Cycle life” *USPTO Application no. 62333782, Pavel Khokhlov, James Kaschmitter, Ernest Demaray, May 2016.*

Comparison with current batteries

On a $/Wh basis

Panasonic 18650	~ $7
H-LTFB	~$50

however

On a $/Wh-cycle basis;

Panasonic 18650	~ 13 cents
h-LTFB	~ *8 cents*

*H-LTFB cell be*nefits;

saves	10 batteries
saves	10 changes
Weight	2.4 x less
Volume	14 x less
Self discharge	years not days
safety	solid state

Cell Performance	Panasonic 18650BE	EnFilm™ thin film µ-battery	hibrid Thin Film high Cap NMC cell
Amp-h	3.2	.7 E^{-3}	3.2
kWh/kg	214	14	500
kWh/L	112	0.008	1500
Ω	0.035	100	0.144
voltage	3.6	3.9	3.7
fDOD cycle life	500	4,000	5,000
self discharge	2%/day	none	none
Wh	10.5	0.003	12.8
$/Wh	$ 0.67	$ 9,000	$ 4.16
cents/Wh-cycle	13 cents	a lot	8 cents

Example Market Applications for the hybrid LTFBcell

- **Satellites** batteries are ~ $500M/yr and are 25% battery weight but only use 25% of their full discharge capacity for higher cycle life. For similar Wh storage the h-LTFBc saves more than 20 % weight, savings ~ $2M/bird launch cost. It frees up replaced volume by 14x for increased payload and increases cycle life by 10x or energy by 10x for similar weight.
- **AN 85kWh Tesla** would go from 1,200lb to 500lb or from 280 miles to 600 miles for the same weight with 14 x less volume and the ability to hold charge indefinitely. It would enable a battery with a replaceable car.
- **Electric flight and drones** would be an early market to benefit from cell performance of the h-LTFB cell. Elon Musk said when 400Wh/kg is available he will start building VTOLs!.
- **iOT sensors and remote/wearable** connected devices is a $4B market growing at ~ 27% CAGR. As energy harvesting and self-charging wireless sensor networks evolve, the solid state TFB already provides uninterruptible power that can continuously recharge or hold a charge for the 5-year life of high margin products.
- **Intermittent renewable solar and wind energy** could be stored over years at a cost less than the cost of dispatch over the grid enabling low cost remote, mobile and independent electric energy for mobile and stationary applications alike.
- **Stationary Energy Storage or a low cost power-wall**. DOE estimates that at ~ $100/kWh and 5000 cycles storage of renewable energy would fall below the cost of transmission over the grid

Thank You

http://sustainableskies.org/mike-friends-hybrid-electric-solution/

Further information is available for customers and channel partners under suitable NDA. Please contact Ernest Demaray: ed@edemaray.com,
+1 650-283-7765 cell/text