Manufacturing Technology of All-Solid-State Thin-Film Lithium Secondary Battery for IoT Applications

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ULVAC, Inc.

Outline

1. All-solid-state thin-film battery contribute to the realization of next generation “Smart Society”
2. Features and applications of thin-film battery as a micro-battery
3. Manufacturing technologies for all-solid-state thin-film battery
4. Recent developments
5. Summary (Future perspective)

Technologies Required for "Smart Systems"

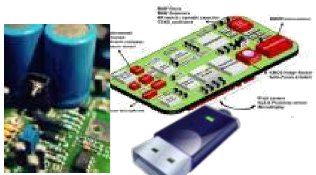
Auto driving | AI/Robotics | AR/VR | Drone | Agriculture | Virtual currency

Google, Microsoft, TOYOTA, IBM, SoftBank, CYBERNET, JIG-SAW, SUN, dji, Parrot, 3DR, ANFF, The University of Queensland Australia, MIZUHO, National Australia Bank, MUFG

Long-life Society

Safety, Security, Medication, Transportation, Communication

Smart functionalities



New ICT

whenever, high-speed, high-volume, safe and secured, low-power-consumption, wireless

Big Data・Cloud Computing

Smart Devices (e.g. Smart Phones)

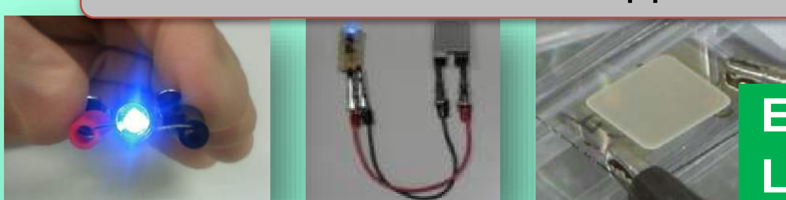
Semiconductor;
Scaling/3D(FEOL/BEOL)
Non-Volatile Memories
Through Silicon Via

Smart Energy

Clean, Safe and High Efficiency

dyson, ilika, SiSOM THIN FILMS

Stand-alone Power Supplies



MEMS/Sensors;
Camera Module
RF Device
Package

Energy;
Li-Battery, Power, Solar cell

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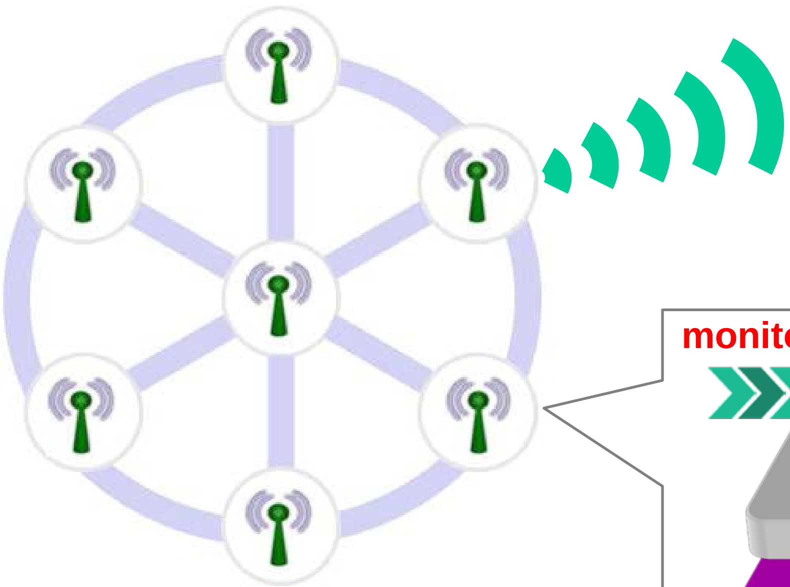
“Smart Systems” Supported Micro-battery

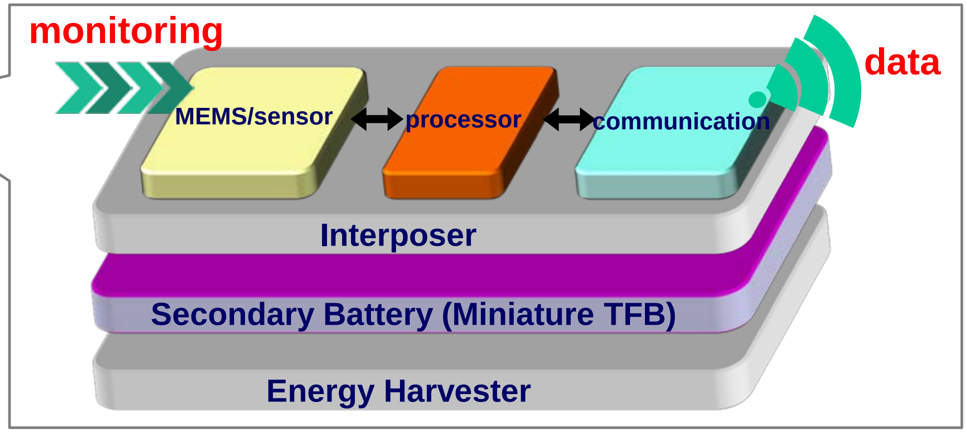
Sensor Node Network



Cloud

Creating a New Value

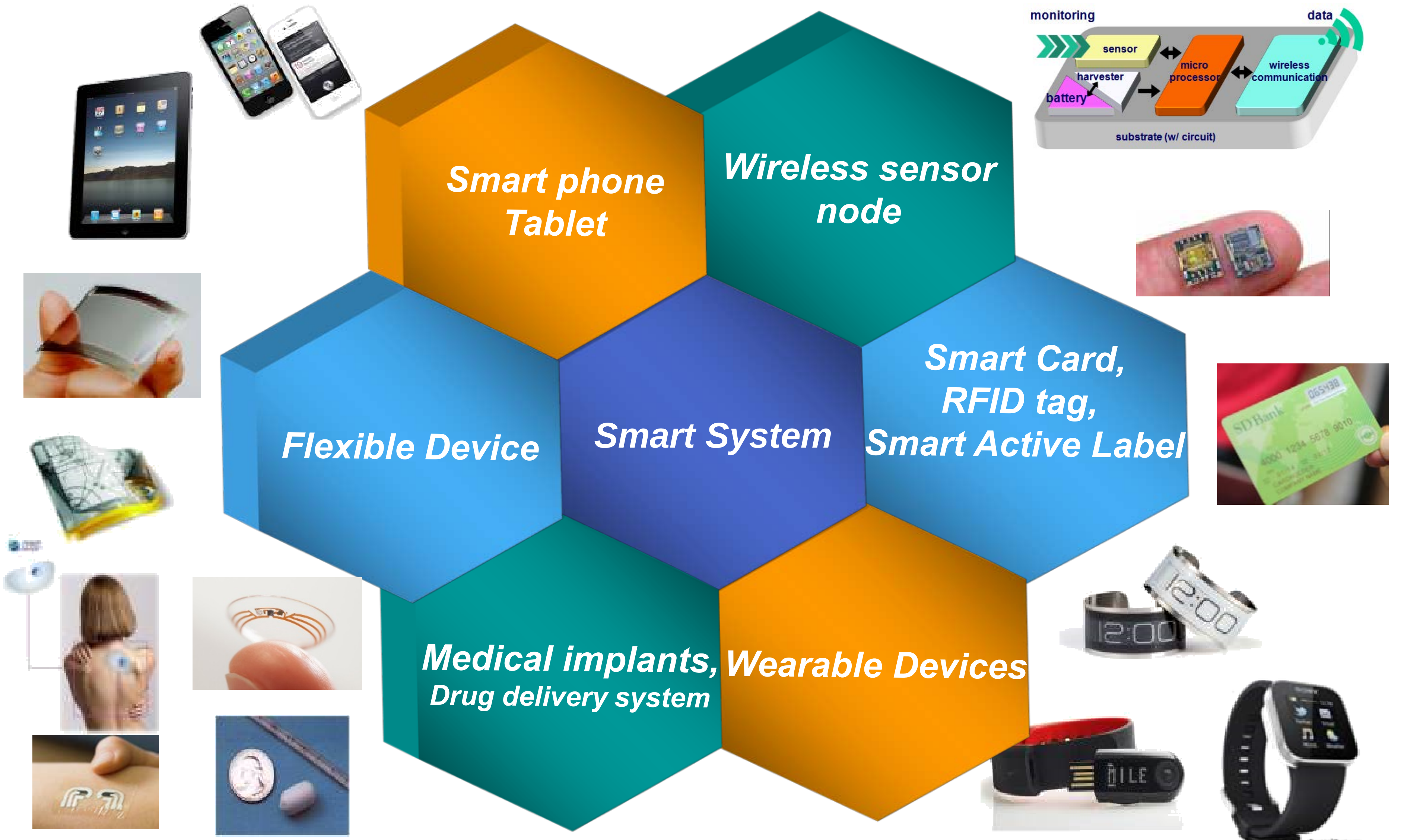
- Industry
- Medical, Health
- Traffic, Distribution
- Life, Amusement
- Infra., Environment



- ☐ MEMS/Sensor (inertial, environmental…)
- ☐ Computer (NVM, processor)
- ☐ Communication (RF module, wireless)
- ☐ Stand-alone Power Supply (TFB + harvester)

\+ Heterogeneous Integration（TSV）

Applications Expected to Li-TFB



Features of Thin-film Battery

1. Ultra-thin, Flexible & Small (thickness < 0.1 mm)
2. Environmental Benign (biocompatibility)
3. Safe (no explosion or overheating : all-solid-state)
4. Flexible Designs (size, shape, etc…)
5. Continuous Power Output (vs. capacitor)
6. High Power Density
7. Long Life & Low Self-discharge (> 10 years)
8. Compatibility with Semiconductor Process
9. High Volume Mass-production Technology

Performance Comparison of Various All-solid-state Li-ion Batteries

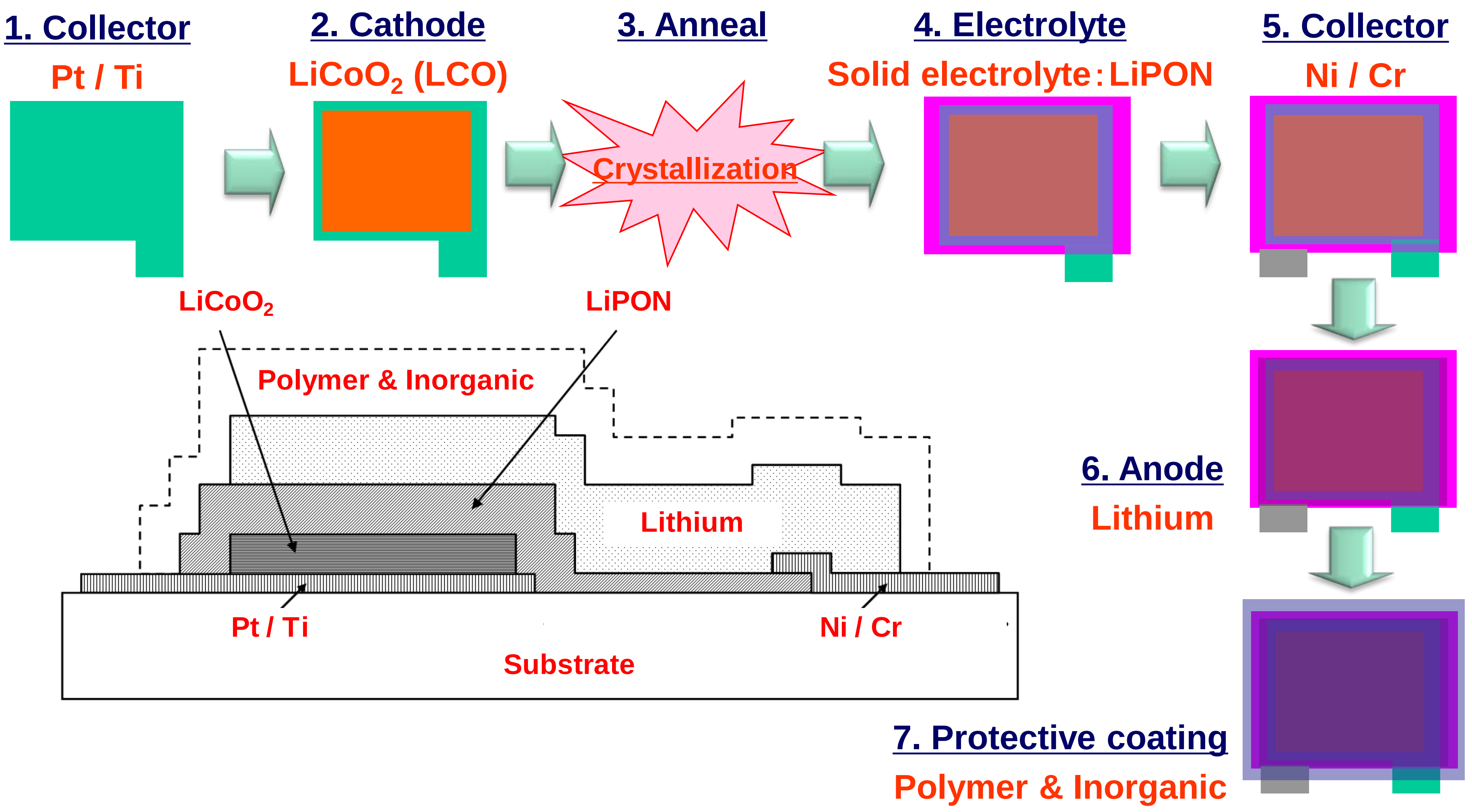
Category	Thin-film Battery (Oxynitride film)	Polymer Battery (Polymer gel)	Polymer Battery (Solid polymer)
Electrolyte	Inorganic glass material (LiPON)	Polymer material (PVDF-HFP system + Lithium salt + Solvent)	Polymer material (PEO + Lithium salt)
Process	Sputtering Evaporation	Coating (Application)	Coating (Application)
Thickness	~0.1 mm	0.3~5 mm	~0.5 mm
Energy density (Wh/L)	~700	~400	~400
C-Rate performance	~30C	~10C	~10C
Temp. performance (deg.C)	-40 to +85	-10 to +60	-10 to +60
Cycle performance	10,000	500	1,000
Charging method	Fast charge (CV)	Standard (CCCV)	Standard (CCCV)
Safety	Safe	Concern	Safe
Cost [BOM] ($/kWh)	1,500	300	300

All solid-state thin-film Li secondary battery is excellent in various performances and most promising to be used as stand-alone power supply for smart ubiquitous devices.

Applications and Required Value of Li-ion Micro-battery

Battery Type	Capacity	Power	Applications
High Capacity	~2,000 mAh	~50 mW	Smartphone, Tablet, Power tool, Toy
Middle Capacity	~300 mAh	~20 mW	Wearable device (Watch, Glass, etc.) Medical device (Pacemaker, Hearing aid, Capsule Endoscope)
Small Capacity	1 μAh~10 mAh	~10 mW	MEMS, Sensors, CMOS memories, Smart card, Drug delivery systems, Medical implantable devices

Device Structure of Li-TFB and Its Manufacturing Process Flow



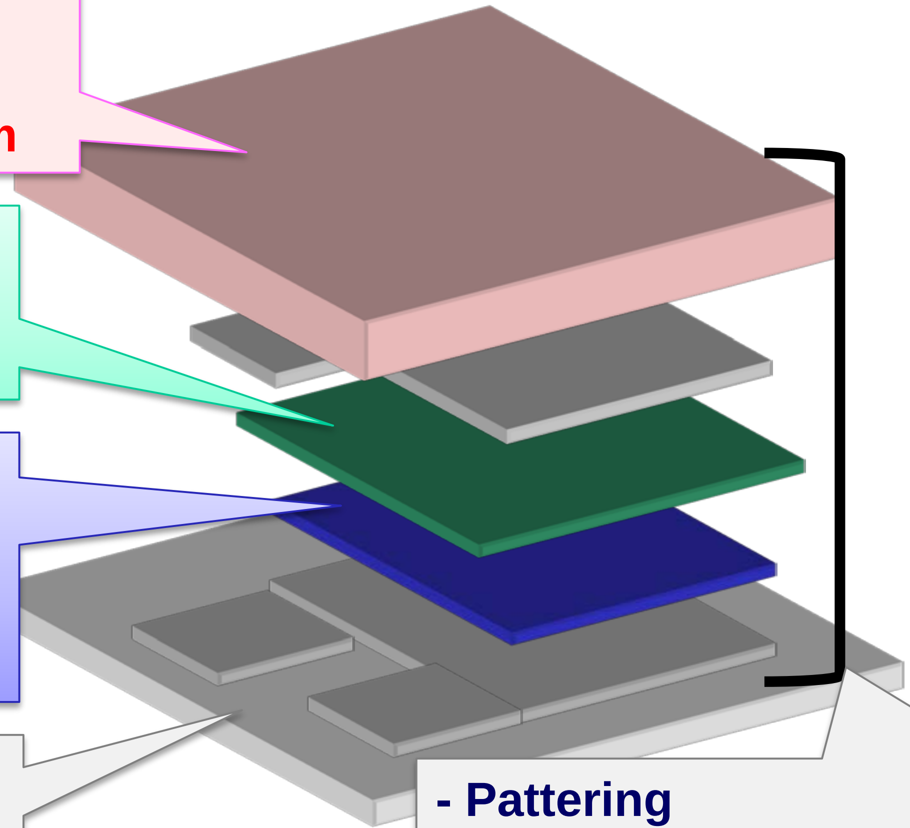
All layers are deposited using mask for patterning.

Technologies, Challenges and Solutions of Li-TFB Manufacturing

- Protective Coating
■VDP and Dielectric sputtering
-> Polymer/inorganic hybrid film

- Solid Electrolyte
■Dielectric sputtering
-> Novel sputtering module

- Cathode
■Dielectric sputtering
-> Novel sputtering module
-> RF+DC hybrid, pulse-DC, AC



- Substrate
■Larger, Thinner
-> In-line sputtering module

- Pattering
■In-situ pattering
-> Mask-through deposition

Development both hardware and process
ULVAC successfully developed mass-production technology.

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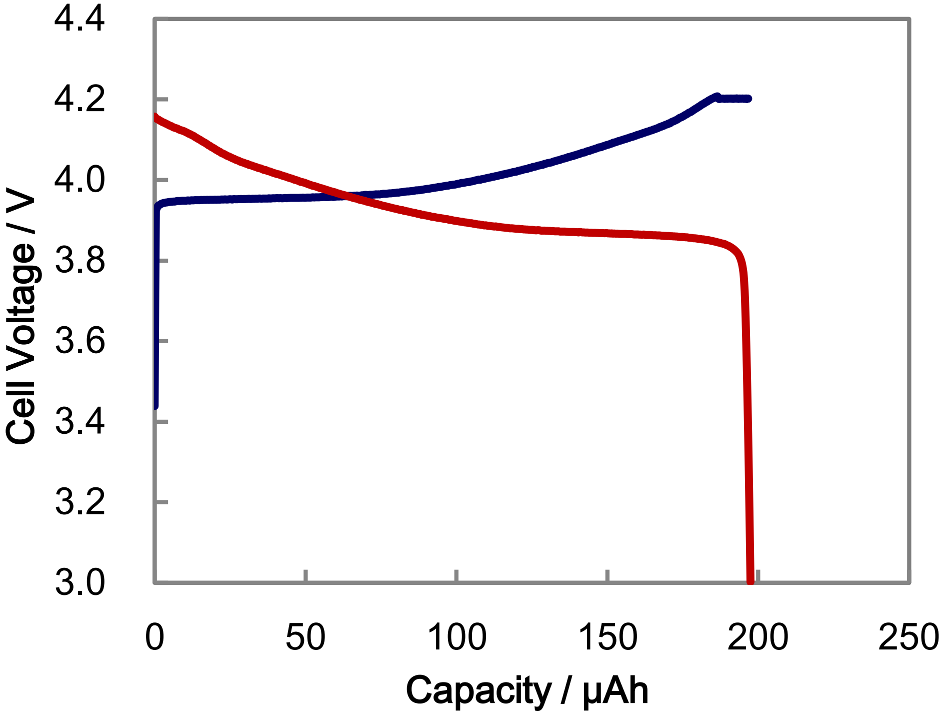
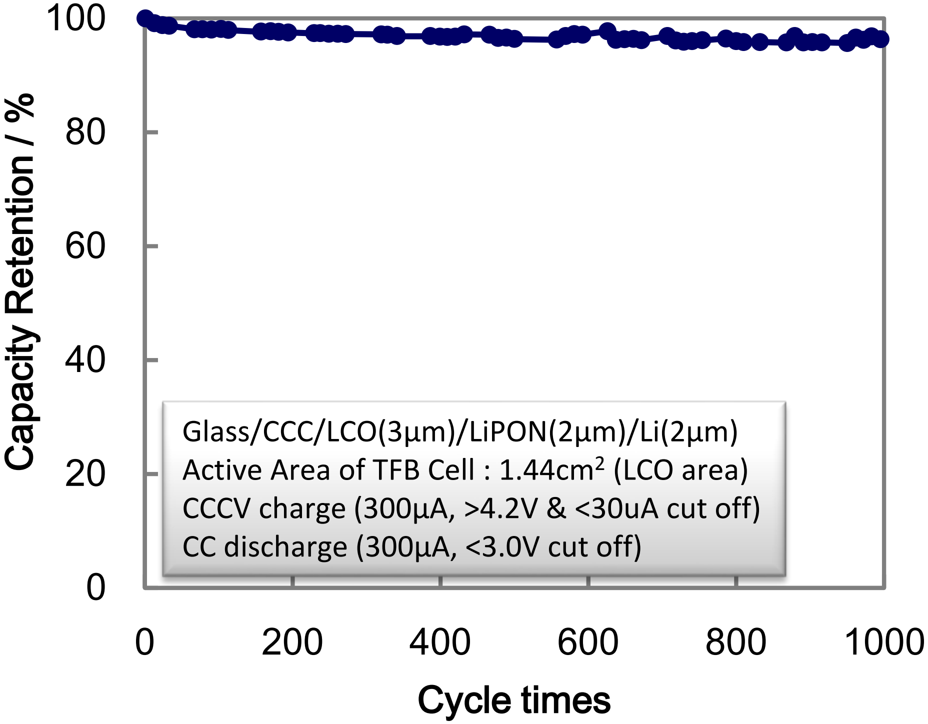
ULVAC Standard Thin-film Battery - Charge/Discharge Curves & Cycle Performance -

Charge/Discharge Curves



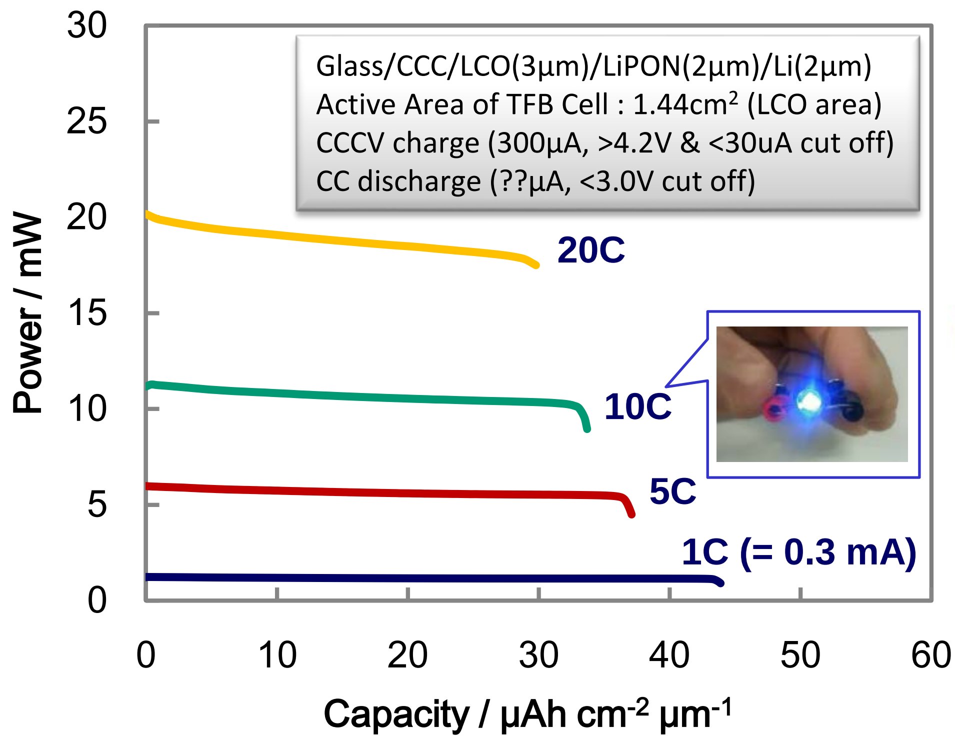
Cycle Performance

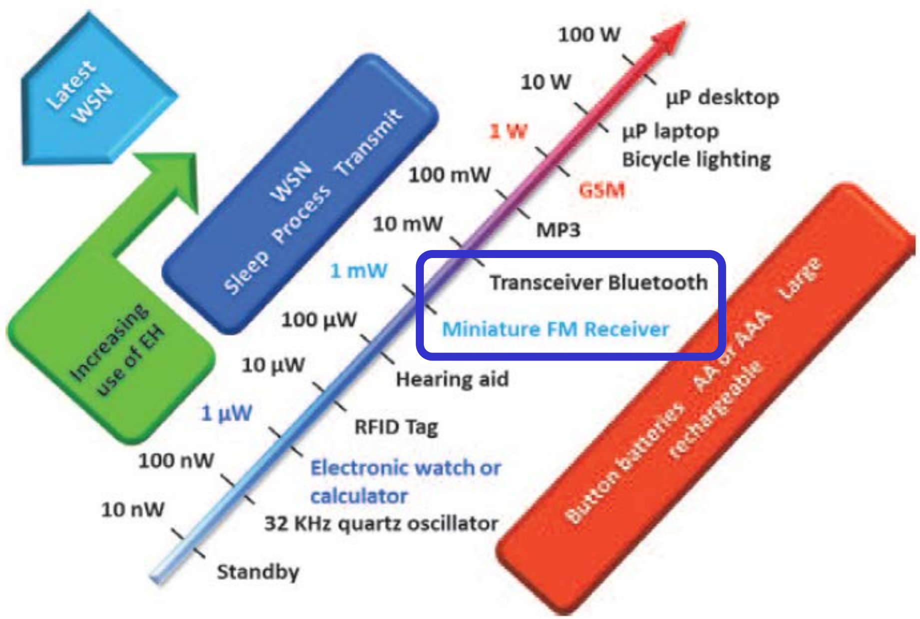


Plateau voltage of discharge has about 3.9 V.

The capacity after 1000 cycles (Depth of discharge : 100%) is about 95%.

ULVAC Standard Thin-film Battery
- Power Performance -





Internet of Things – Converging Technologies for Smart Environments and Integrated Ecosystems,
River Publishers Series in Communications.

Constant power can be applied under each discharge condition, and “Bluetooth LE” and “FM receiver” can be operated.

ULVAC Standard Li-ion Micro-battery
- Safety Test -

Short-circuit Test

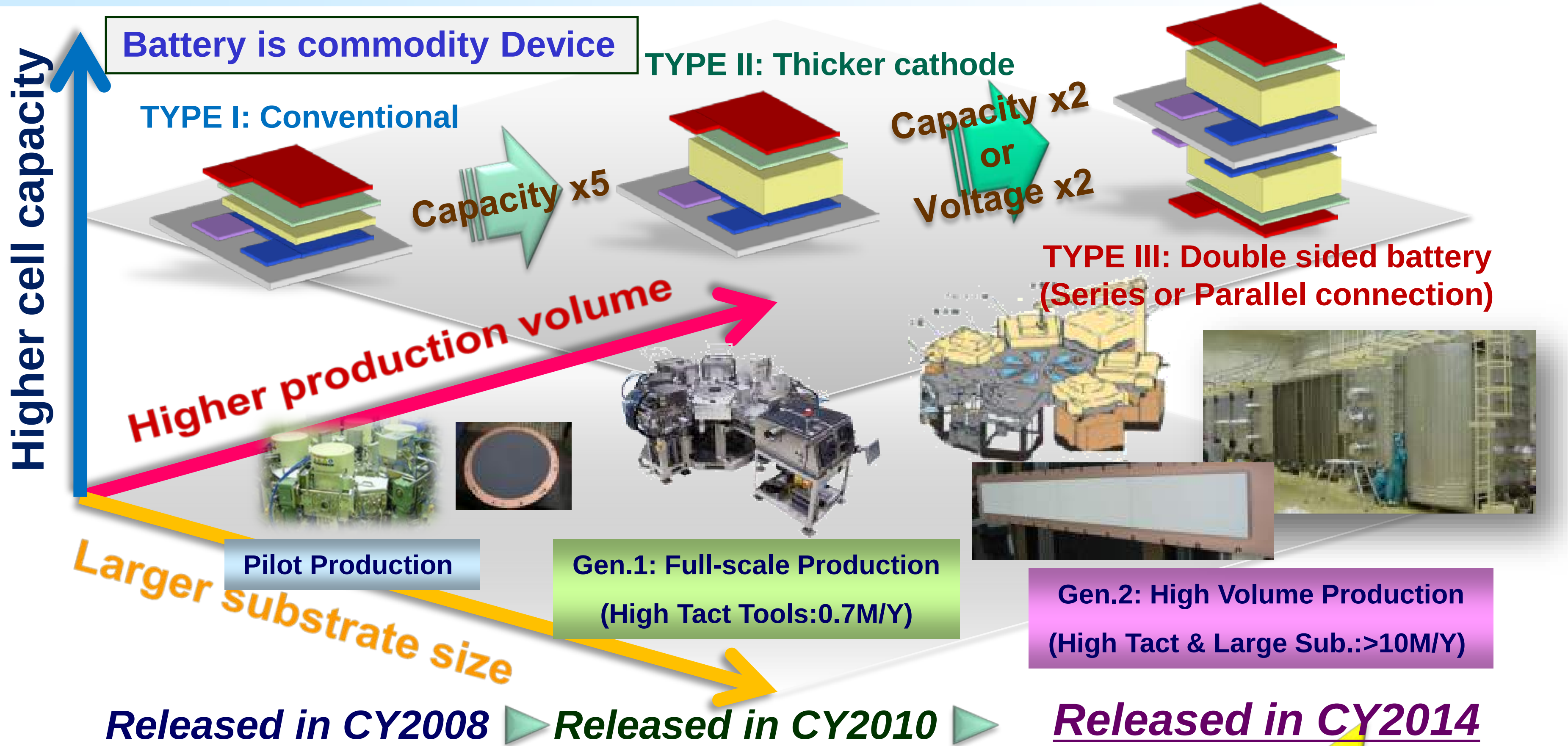
Before Nailing   After Nailing

No change was observed even after nailing test.
Reaction proceeded slowly from electrically shorted part.

Soaking Test (put into water)

Vigorous reaction of Li and water cannot be seen and reaction proceeded slowly from cracked part.

Roadmap of Li-ion Micro-battery Production



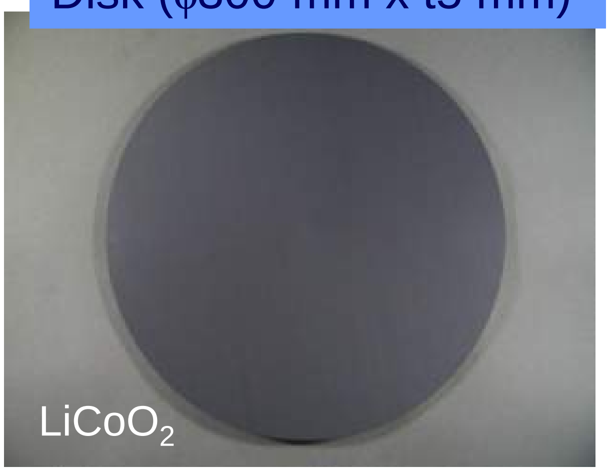
Our strengths of being both FPD/Solar Cell and Semiconductor equipment supplier.

- ✓ **FPD/Solar Cell -> Large substrates Sputtering.**
- ✓ **Semiconductor -> High-quality fine-cell fabrication.**

- ■**Cost-effective**
- ■**High-performance**
- ■**Large-scale**

Development of Mass Production Technology
- Large Rectangular Target for Gen.2 Line -

Disk (ϕ300 mm x t5 mm)



Pilot, Gen.1 Line

Rectangular (110 mm x 1040 mm x t6 mm, etc.)

Gen.2 Line

Development of Mass Production Technology
- In-line Sputtering System for Gen.2 Line -

Cluster system

Cathode : only 1 pcs/chamber
Target shape : disk
Target size > Substrate
Substrate : static

In-line system

Cathode : > 2 pcs/chamber
Target shape : rectangular
Target size < Substrate
Substrate : dynamic

In-line system including know-how obtained in the cluster system

Recent Material Developments

- **Cathode Material**
  - **1. Higher voltage and capacity**
    - $LiCoO_2$ => $Li[NiCoAl/NiCoMn]O_2$, $Li_{1+x}MnO_2$
  - **2. Low-temperature process**
    - $LiCoO_2$ => $LiMn_2O_4$
- **Electrolyte Material (for higher ionic conductivity)**
  - ✓ Mixed anion effect : Li_3PO_4 - α(Li_4SiO_4, Li_3BO_3, etc…)
  - Sulfur based materials (e.g. Li_2S-P_2S_5)
- **Anode Material (for high temperature-resistant)**
  - ✓ Li alloy (e.g. Si, SnO_2, etc…)
- **Advanced Approach**
  - LCO surface modification layer (for reducing interfacial resistance)
  - Engineered composite particles for improving both ionic and electronic conductivities. (JDP with Sisom Thin Films LLC)

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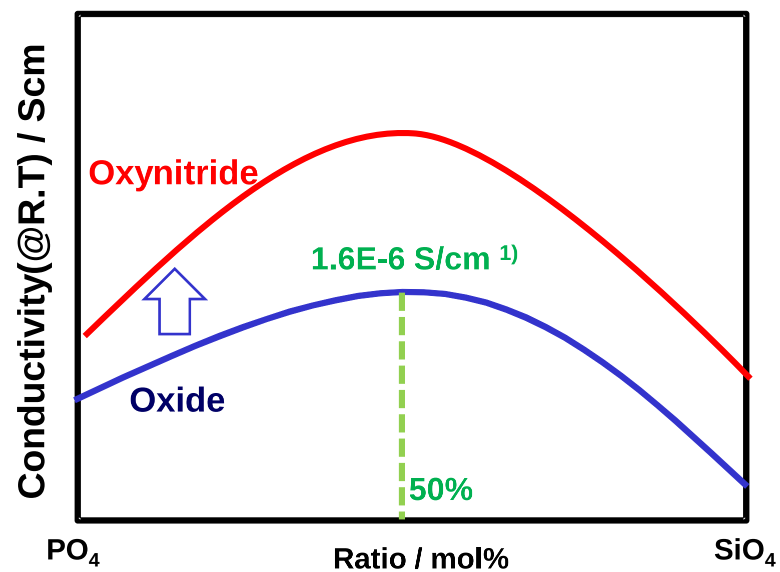
Improvement of Ionic Conductivity with Mixed Anion Effect

It has reported that Li-ion conductivity is improved by mixing another anion unit[1-6].

	Li_3PO_4	Li_3BO_3	Li_4SiO_4	Li_3VO_4
Li_3PO_4	5.1x10^{-7} (1)			
	1.5x10^{-6} (8)			
Li_3BO_3	1.2x10^{-7} (2)	1.0x10^{-7} (6)	6.0x10^{-6} (4)	
		2.3x10^{-6} (7)		
Li_4SiO_4	**1.6x10^{-6} (1)**		1.2x10^{-8} (1)	
	3.7x10^{-6} (8)			
Li_3VO_4	1.1x10^{-6} (3)		2.5x10^{-7} (5)	



oxide data

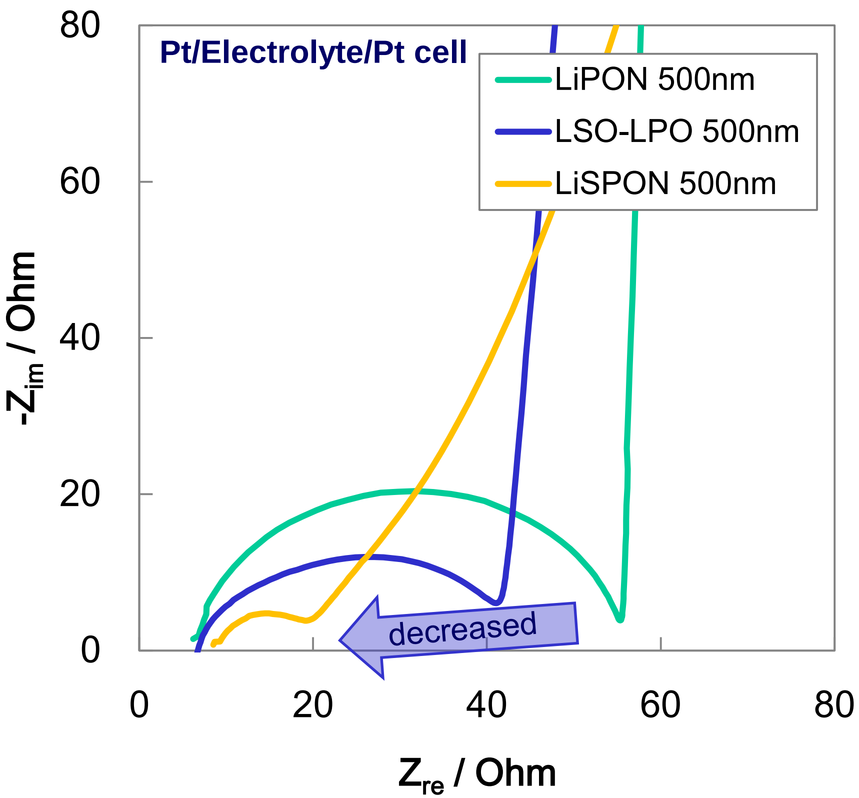
oxynitride data

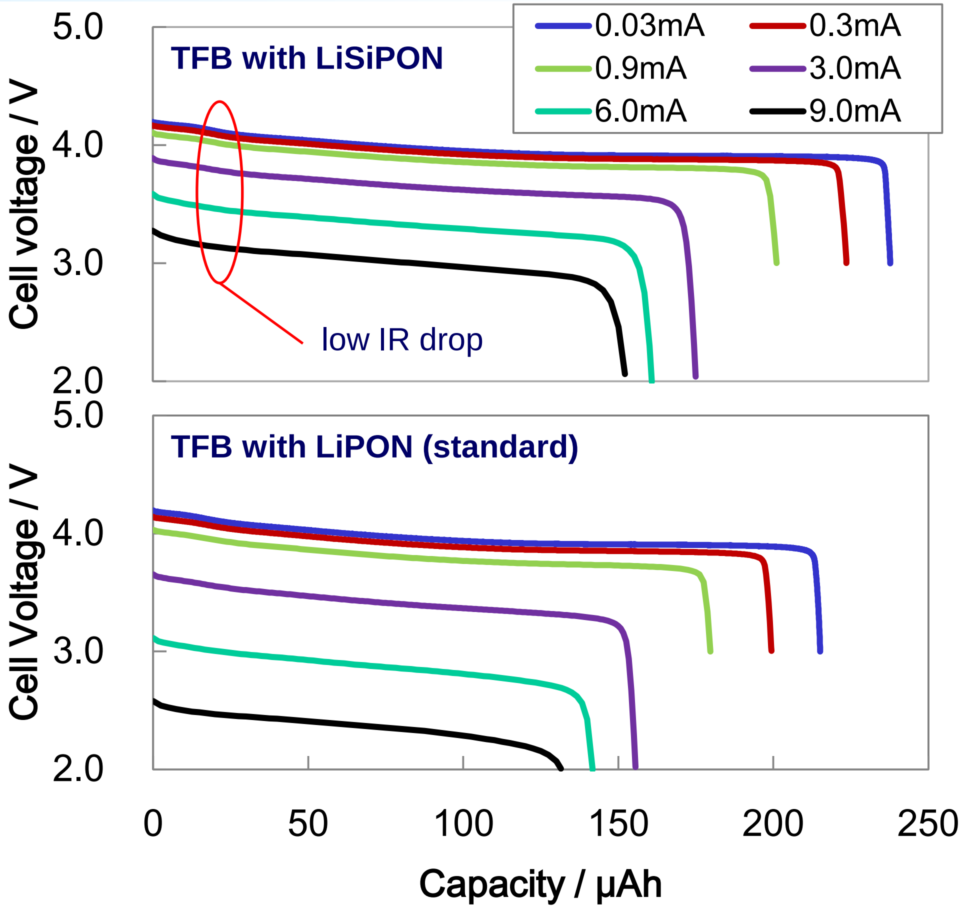
1) Y. Sakurai, A. Sakuda, A. Hayashi, M. Tatsumisago, Solid State Ionics, **182** (2011) 59.
2) S. Lee, J. Kim, D. Shin, Solid State Ionics, **178** (2007) 375
3) J. Kawamura, et al, Symposium on Solid State Ionics in Japan **32nd** (2006) 124
4) M. Tatsumisago and T. Minam, Mater. Chem. Phys, **18** (1987) 1
5) N. Kuwata, J. Kawamura, K. Toribami, T. Hattori, N. Sata, Electrochemistry Communications, **6** (2004) 417
6) Y. Ito, K. Miyauchi, T. Oi, J. Non-Cryst. Solids, **57** (1983) 389
7) J.M.Kim, G.B.Park, K.C.Lee, H.Y.Park, S.C.Nam and S.W.Song, Journal Power Sources **189** (2009) 211.
8) ULVAC internal data

Further higher conductivity might be expected by forming oxynitride glassy electrolyte with mixed anion.

Possibility of LiSiPON Electrolyte
- Ionic Conductivity and Power Characteristics -

* LPO-LSO : Li_3PO_4-Li_4SiO_4





Ionic conductivity of LPO-LSO oxynitride can be estimated to 3.7E-6 S/cm. Power characteristics of TFB with LiSiPON is more improved than that of standard TFB with LiPON.

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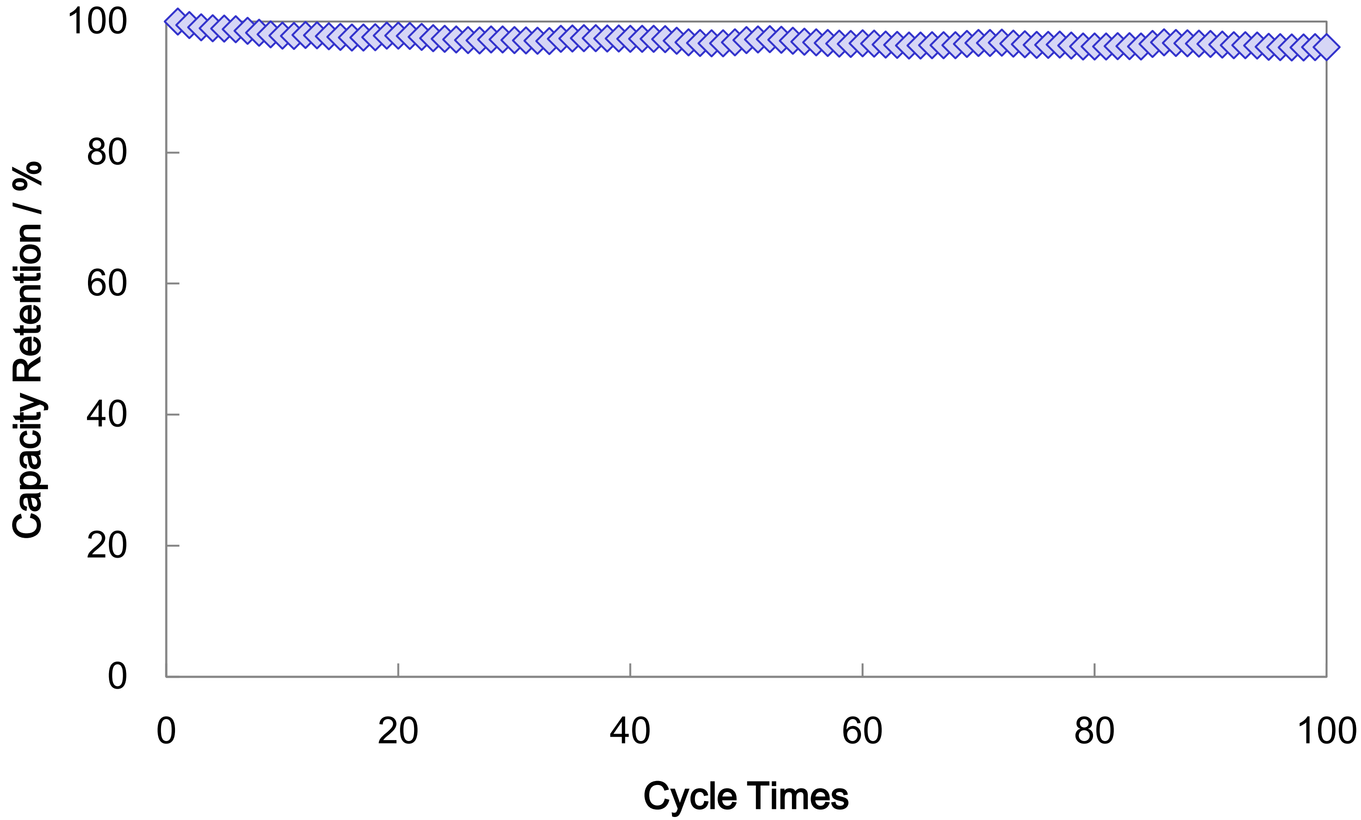
Possibility of LiSiPON Electrolyte
- Cycle Performance -



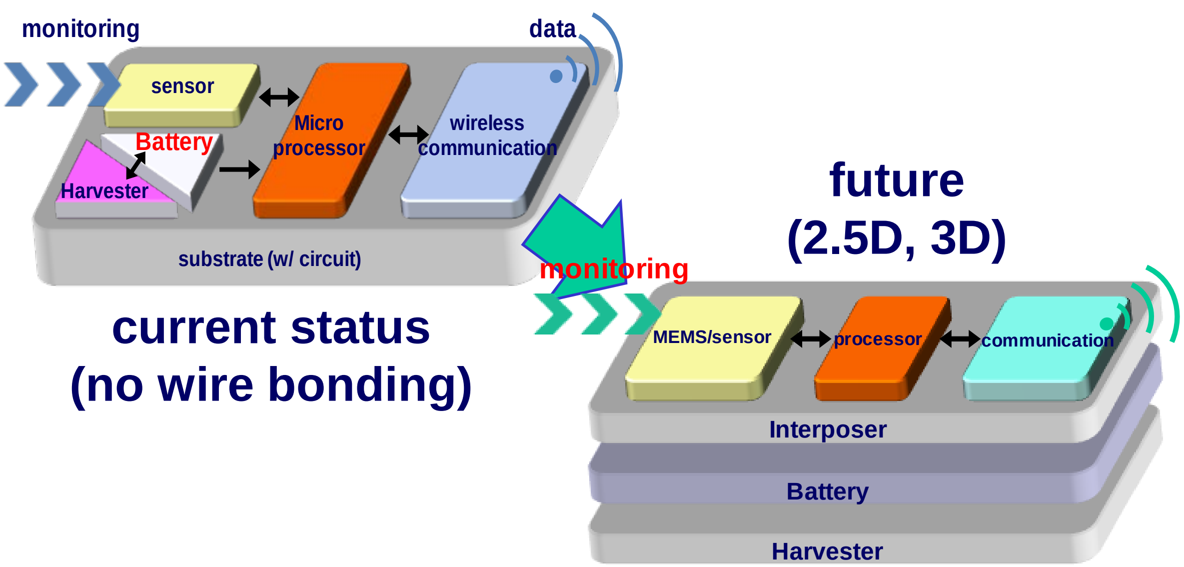
TFB with LiSiPON electrolyte results good cycle performance as same as standard TFB.

High-density Packaging with TFB

Next Generation IoT Device

- MEMS/Sensor (inertial, environmental…)
- Computer (NVM, processor)
- Communication (wireless)
- Stand-alone Power Supply (TFB + harvester)

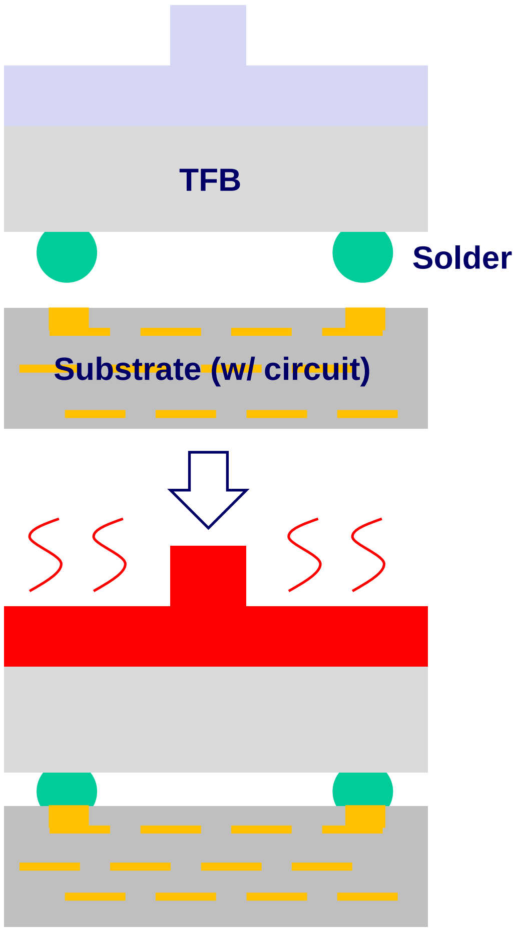
High-density Packaging



current status
(no wire bonding)

future
(2.5D, 3D)

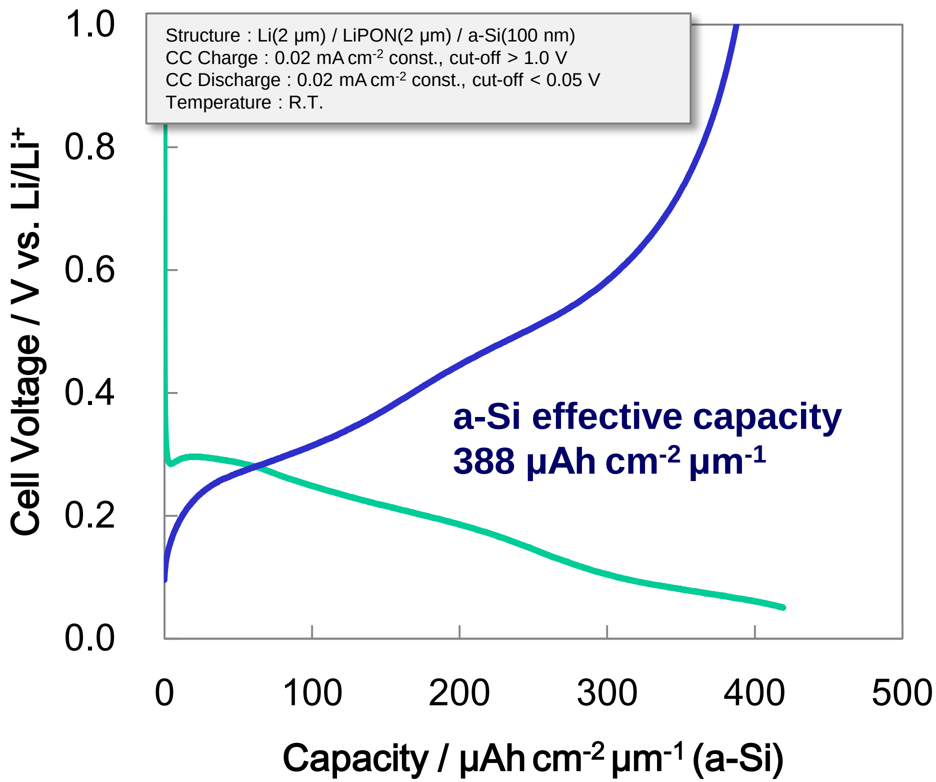
Issue of TFB Mounting

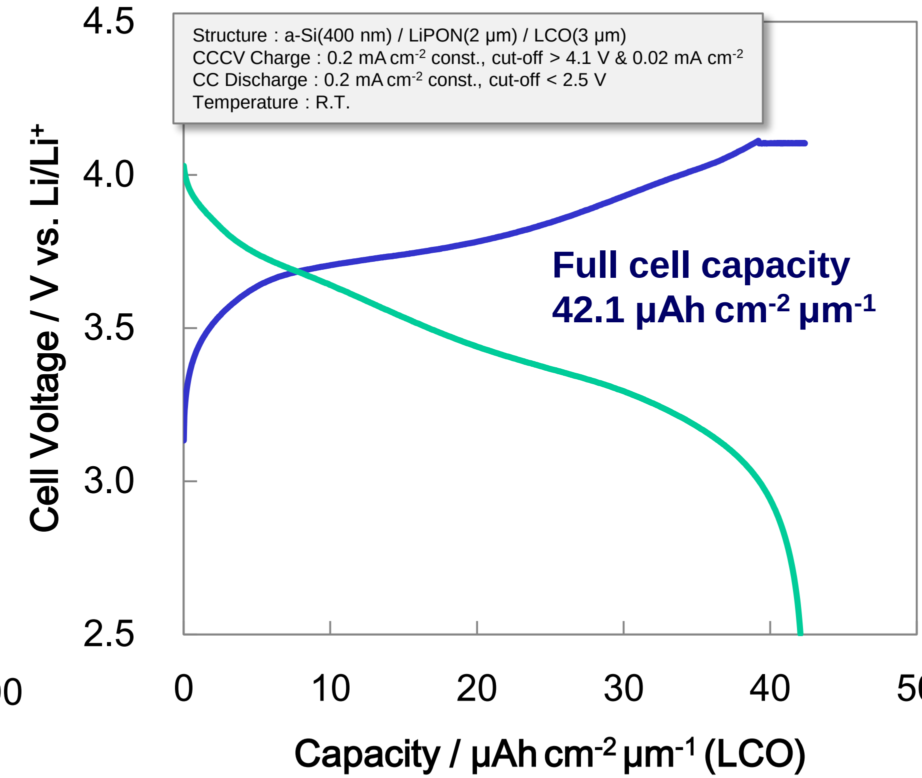


Solder reflow : ~250 deg.C
(Li melting point : 180 deg.C)

Li-free Anode for High-temperature Tolerance
- Basic Performance with a-Si Electrode -

Li/LiPON/a-Si half cell → a-Si/LiPON/LCO full cell





TFB with a-Si anode is formed by optimizing thickness ratio between cathode and anode.

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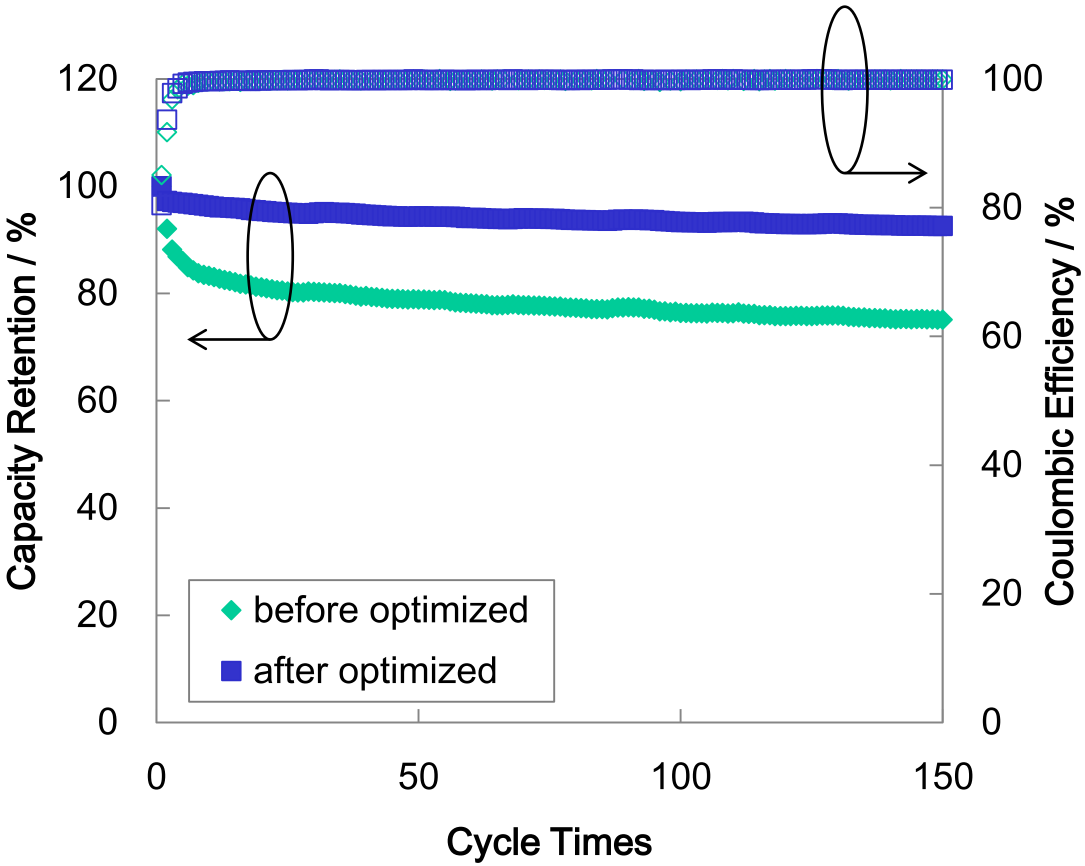
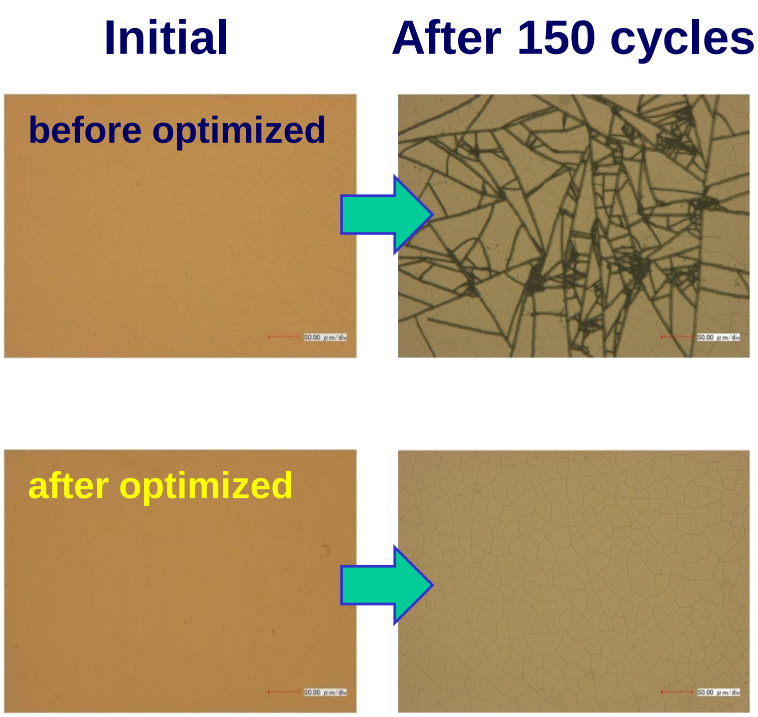
Li-free Anode for High-temperature Tolerance
- Cycle Performance of a-Si/LiPON/LCO Full Cell -



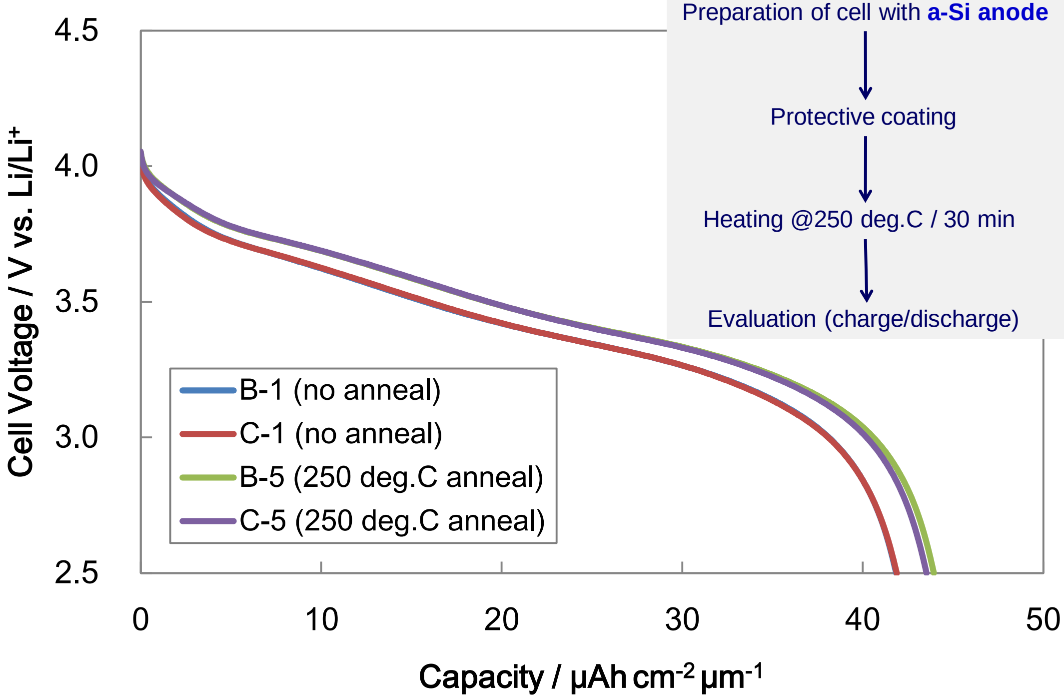
Appearance of anode surface



Good cycle performance is observed without hard cracks by using porous a-Si anode in order to suppress the electrode breakage.

Li-Free Anode for Higher-temperature Tolerance
- High-temperature Storage Test-

Si/CCC/LCO(3 µm)/LiPON(2 µm)/a-Si(0.4 µm)
CC charge (0.3 mA const., cut-off > 4.1 V & <30 µA)
CC discharge (0.3 mA, cut-off < 2.5 V)



Preparation of cell with **a-Si anode**

↓

Protective coating

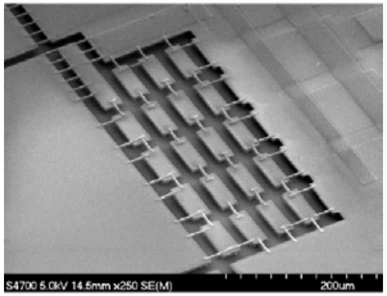
↓

Heating @250 deg.C / 30 min

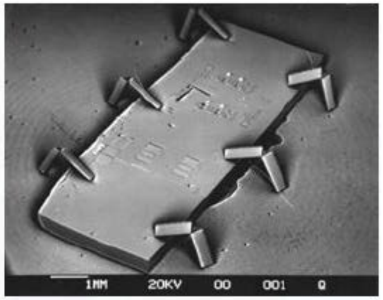
↓

Evaluation (charge/discharge)

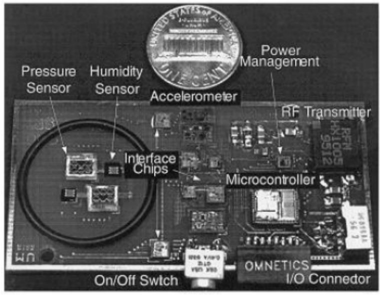
Application



Micro PV (Tokyo Univ.)



Microrobotics (Univ. of California)



Microsystems (Univ. of Michigan)

No degradation was observed after high temperature process.

=> expected to apply to micro devices with high-density packaging

Future Prospects of Li-ion Micro-battery - Development Roadmap (Summary) -