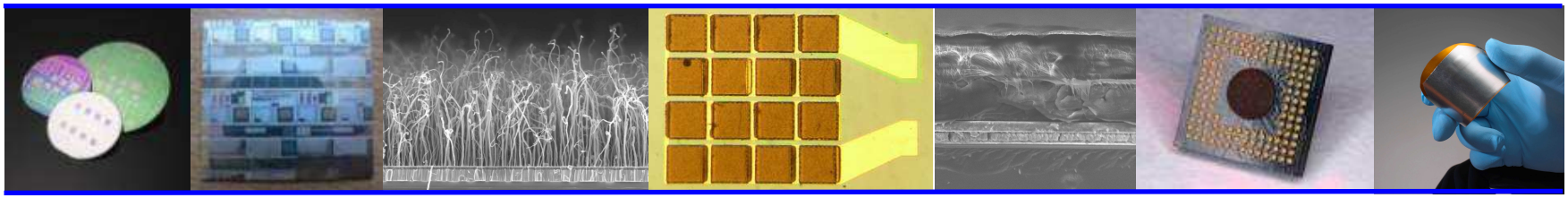


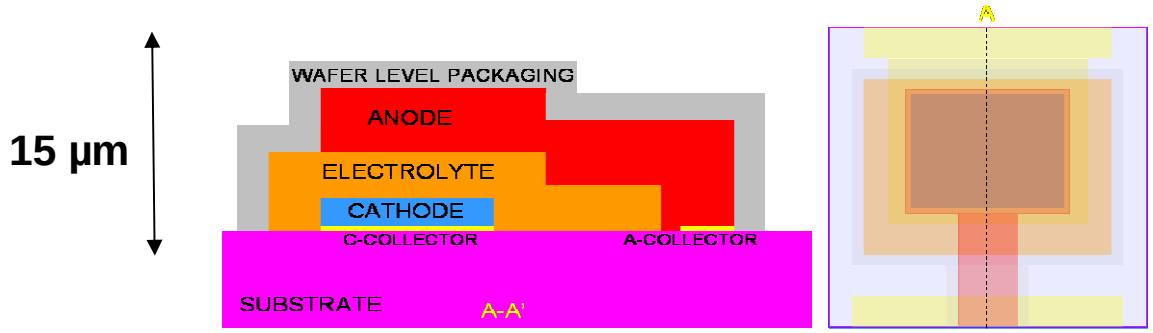
Microstockage d'énergie
Les dernières avancées

S. Martin
(CEA-LITEN / Grenoble)

Outline

- **What is a microbattery?**
- **Microbatteries developped at CEA**
  - Description
  - Performances
  - Integration and Demonstrations
  - On going developements
- **Overview of worldwide developments**
  - Main competitors
  - Prototypes

What is a microbattery ?

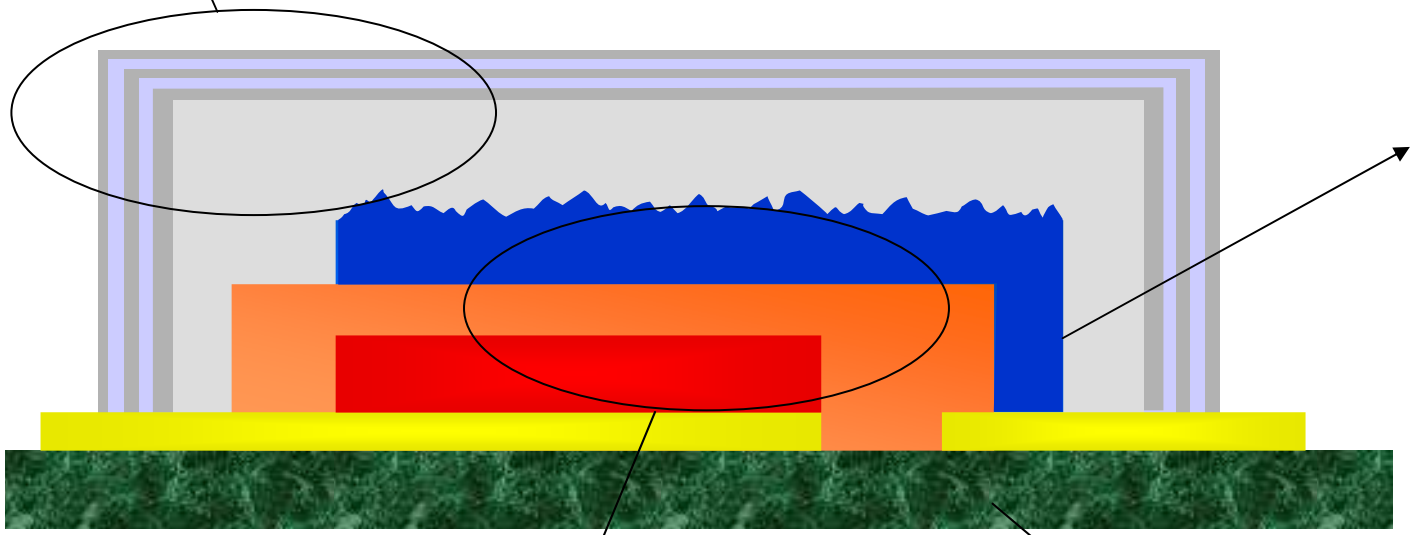


- **Lithium battery**
  - Physics similar to classical lithium battery
- **Solid state battery**
  - No liquid: glassy lithiated electrolyte
- **Thin film battery**
  - Overall thickness : 5-20 µm
  - Realized with thin film deposition facilities

Main developments at CEA

Integration
(QFN Package, autonomous sensors, µUAV…)

Encapsulation
Barrier properties
Flexibility



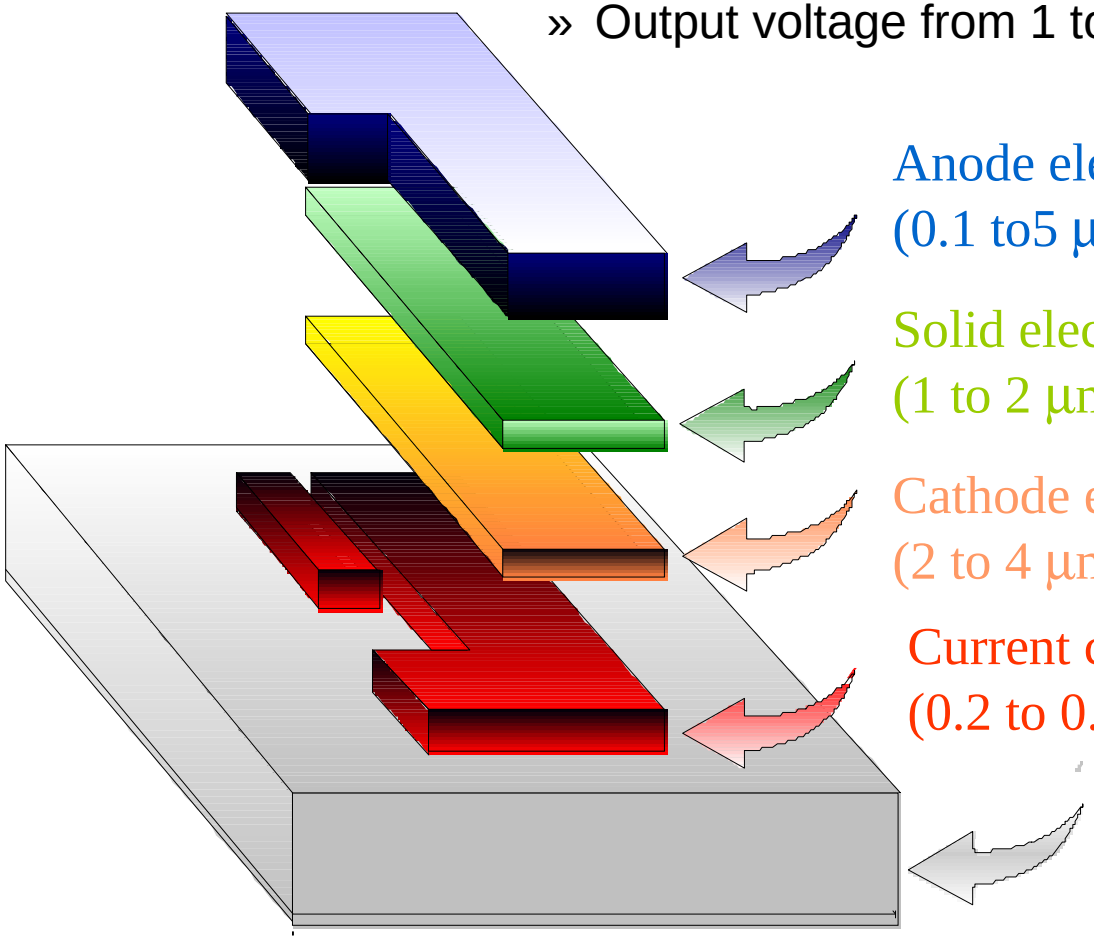
Patterning
Shadow Masks
Maskless Process

Active Stack
Materials
Process

Substrate
Texturation
Flexibiliy

Active stack

- **Different solutions to fit requirements**
  - » Li metal or Li-ion
  - » Low Temperature process
  - » Output voltage from 1 to 4 V



Anode electrode Li, Si_xGe_{1-x}
(0.1 to5 µm), thermal evaporation or sputtering

Solid electrolyte LiPONB
(1 to 2 µm), sputtering

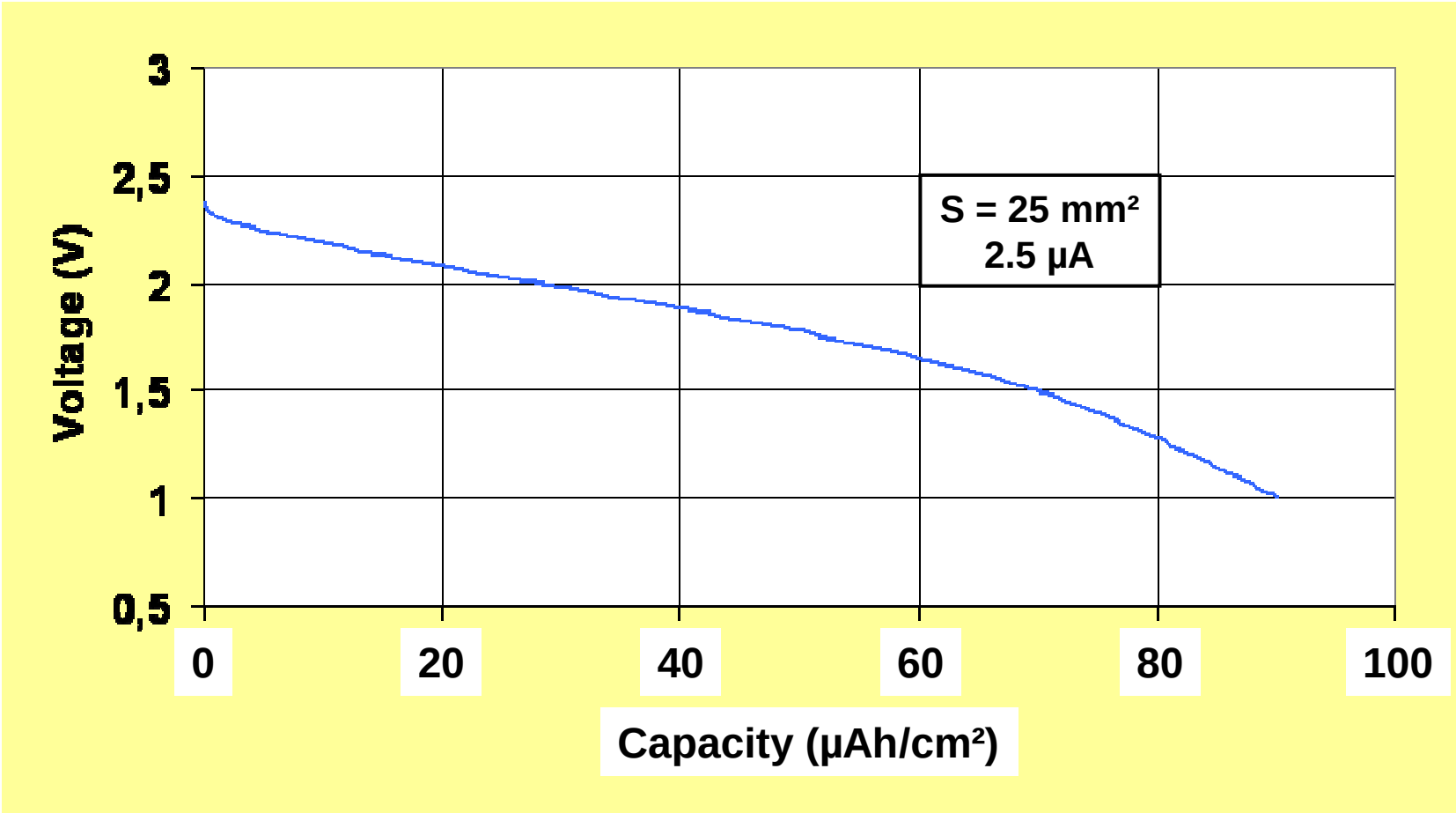
Cathode electrode TiS_xO_y , $LiCoO_2$, V_2O_5
(2 to 4 µm), sputtering

Current collector W, Ti, Pt
(0.2 to 0.5 µm), sputtering

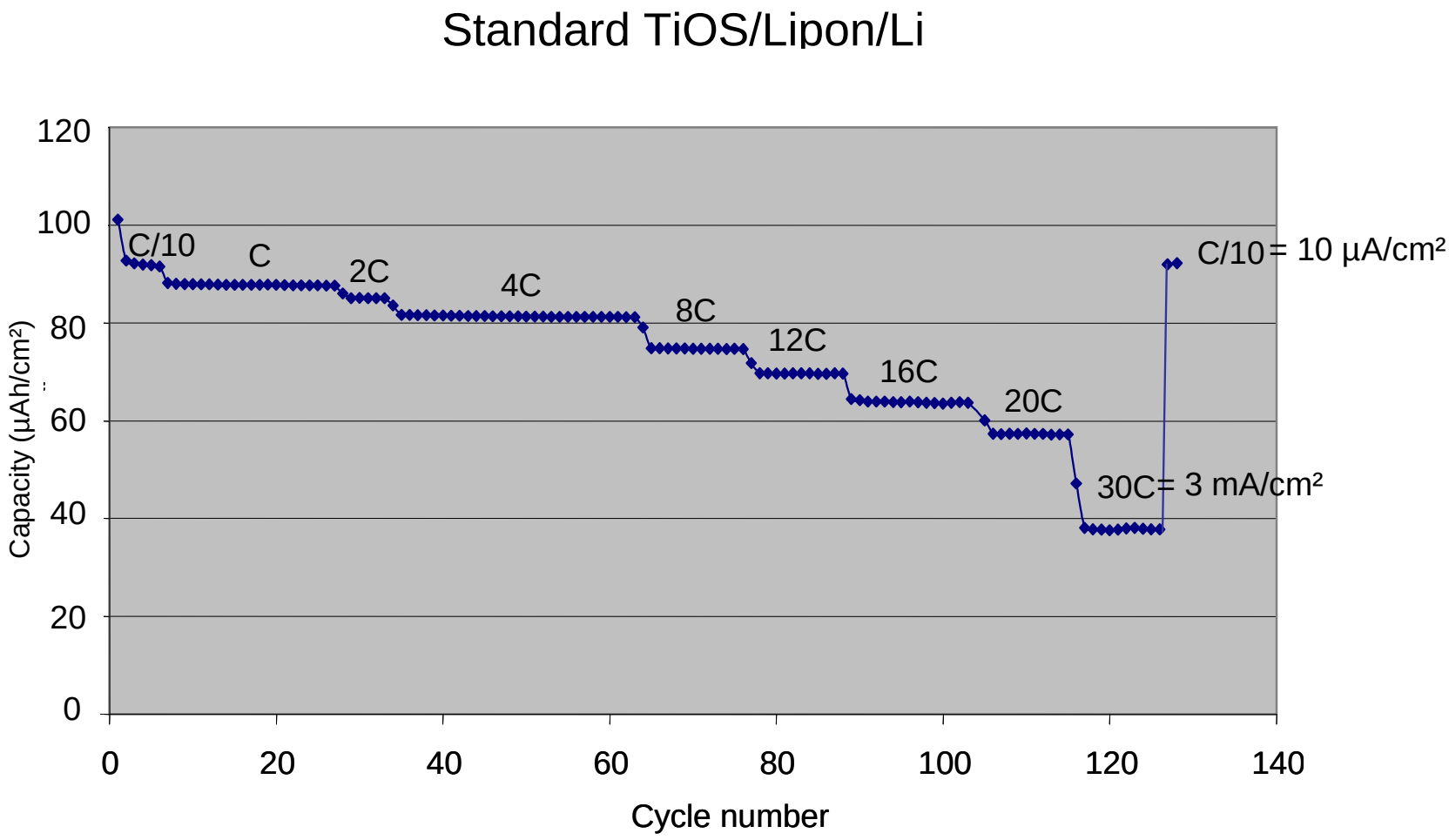
Substrate 4 to 8” Si wafers
Polymers, Ceramic

Microbattery Performance

Standard TiOS/Lipon/Li

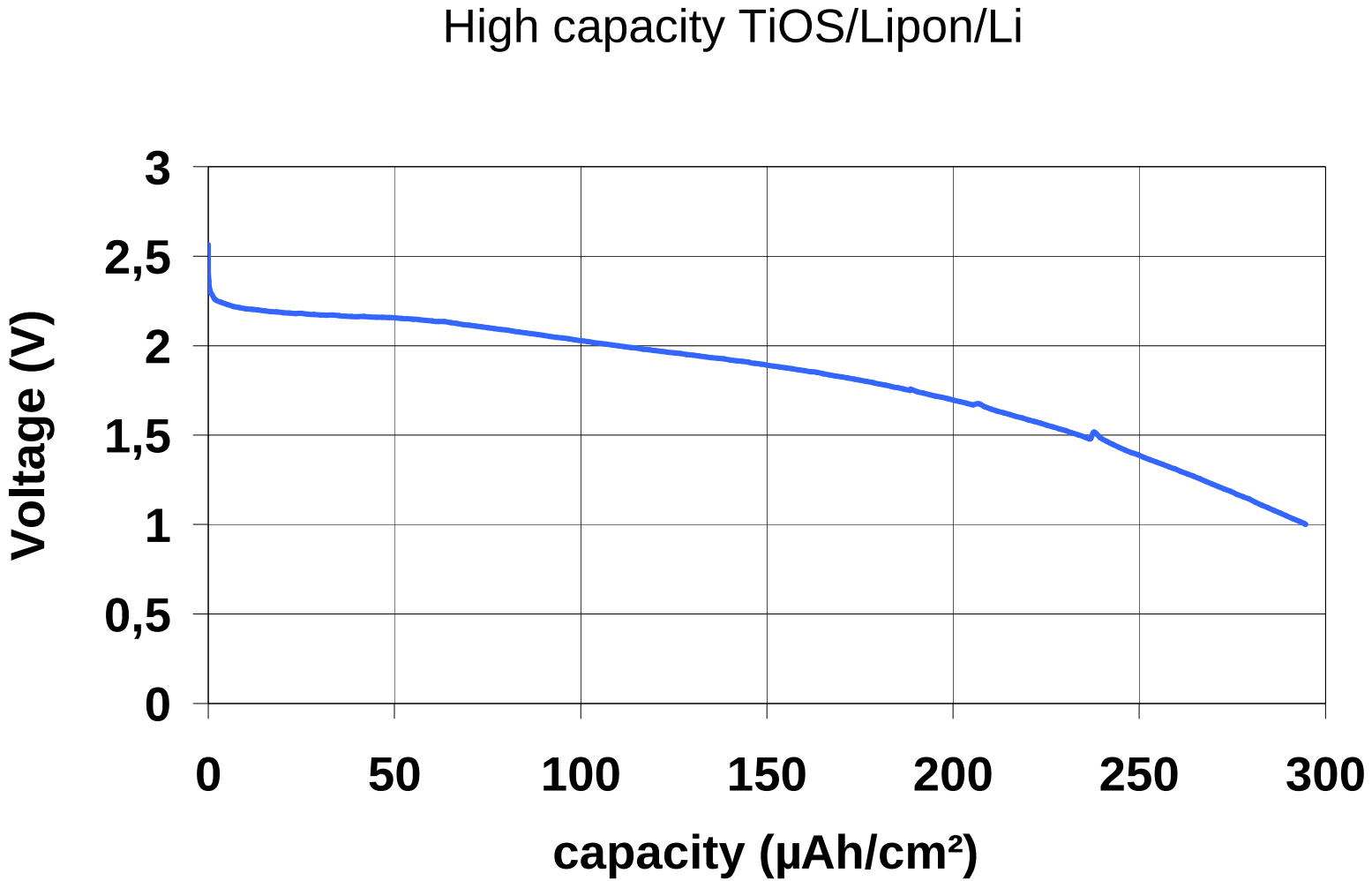


Microbattery Performance



10 µA/cm² during 10 h → **3 mA/cm² during 50 s**

Microbattery Performance

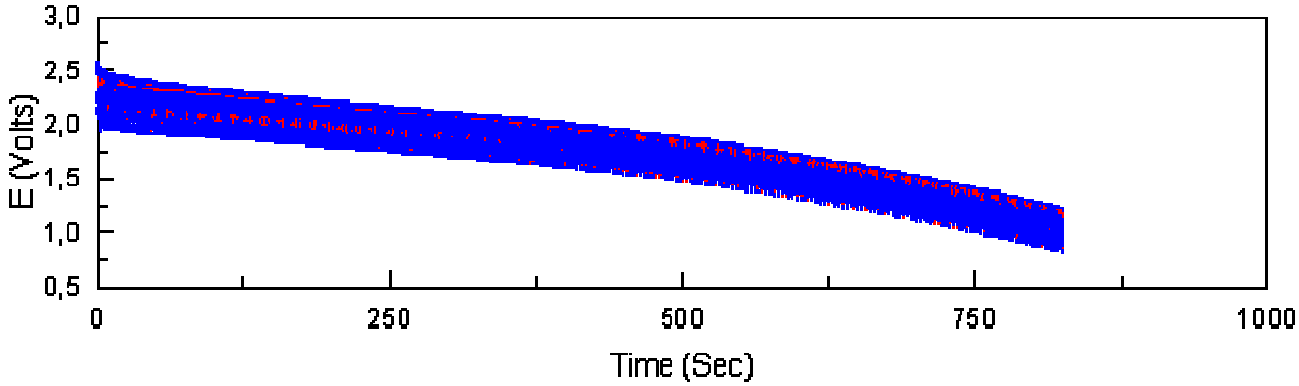


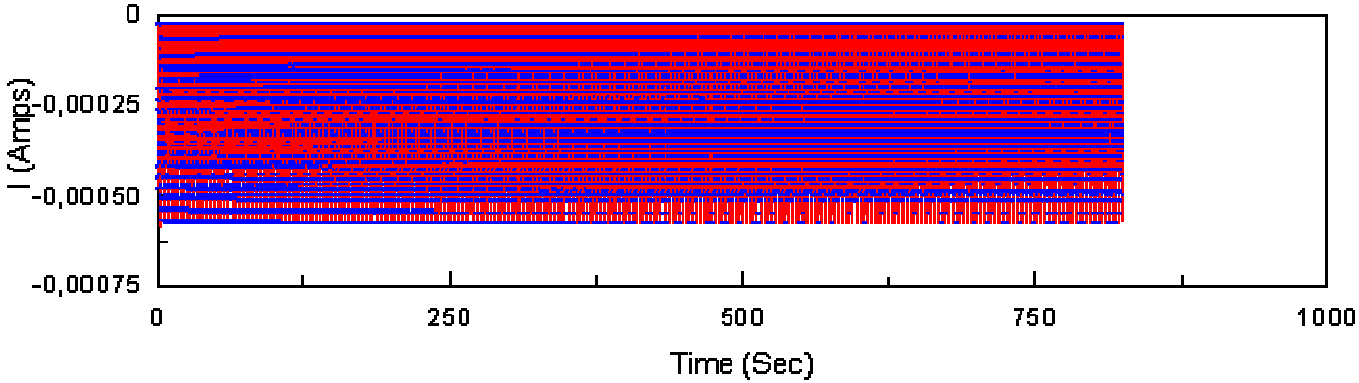
Microbattery Power capability

High duty cycles

Standby current: 25 µA

Pulse current: 2.5 mA/cm^2





Result

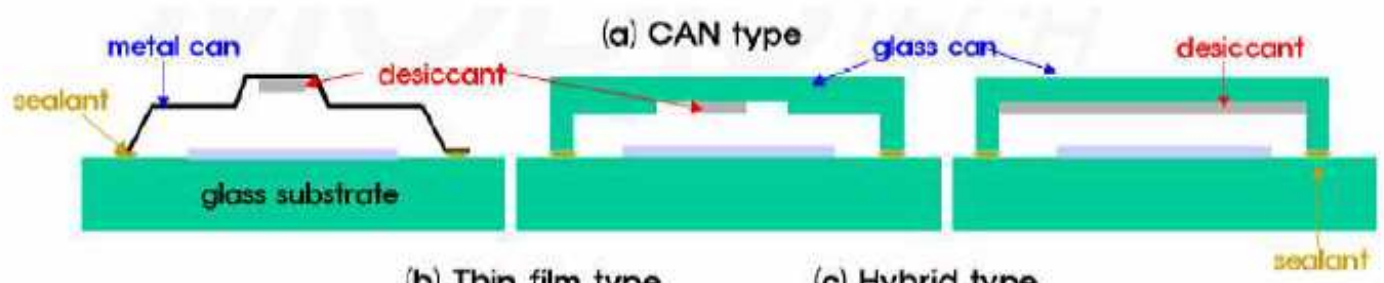
- 4080 High duty cycles
- 28 µAh/cm^2 to 1V discharge

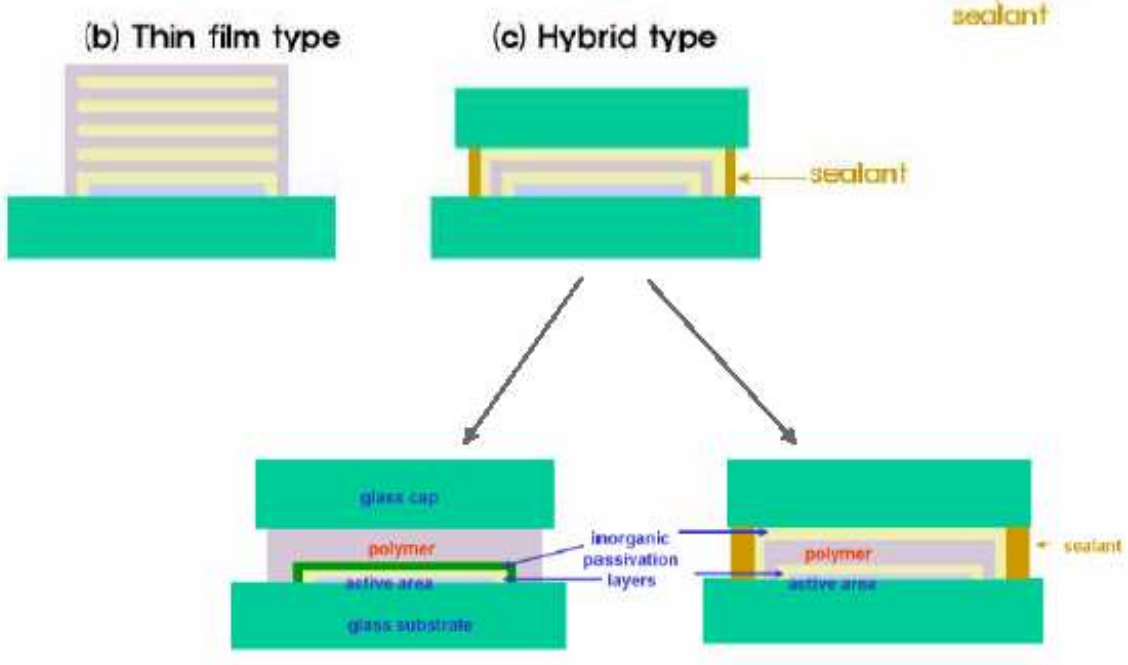
Encapsulation

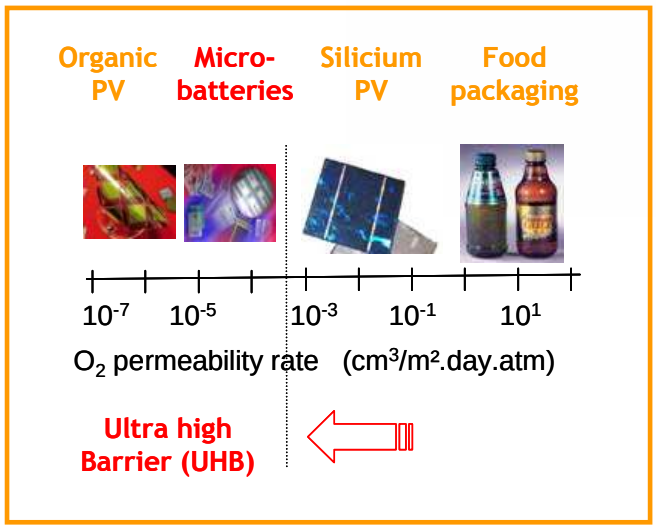
➢3 different routes (possibility to hybride solutions)

➢ Can, thin film, lamination

Influence on Tmax, flexibility, thickness

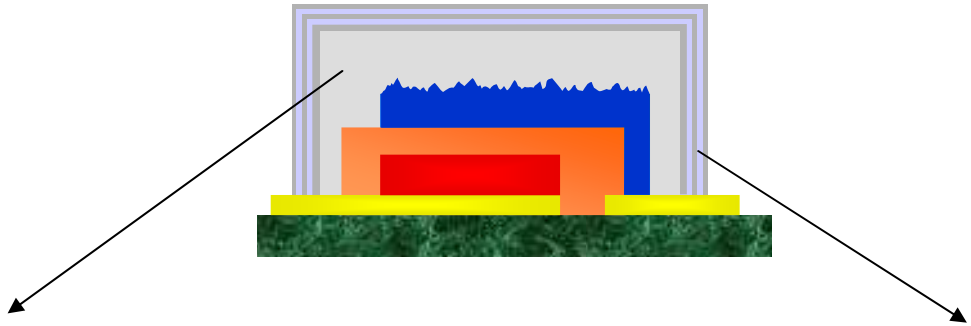






Microbattery encapsulation: thin film solution

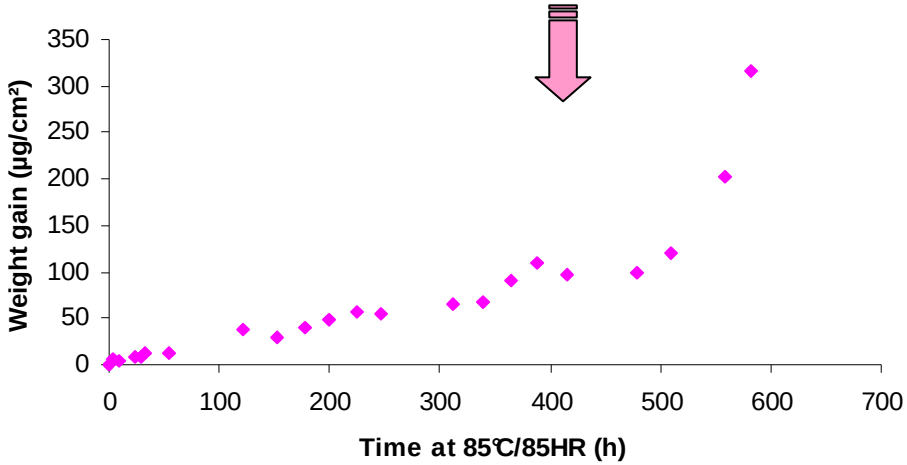
- Strategy: Stack of thin layers with specific characteristics

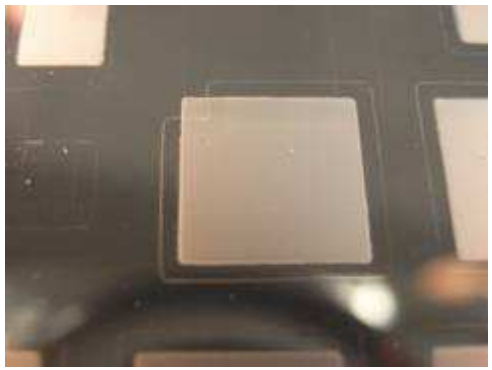


Buffer layer ~ 5 – 10µm
Passivation,Planarization

+

Multilayers barrier (metal or dielectric) ~ 0.5 – 2µm
O_2 and H_2O diffusion barrier



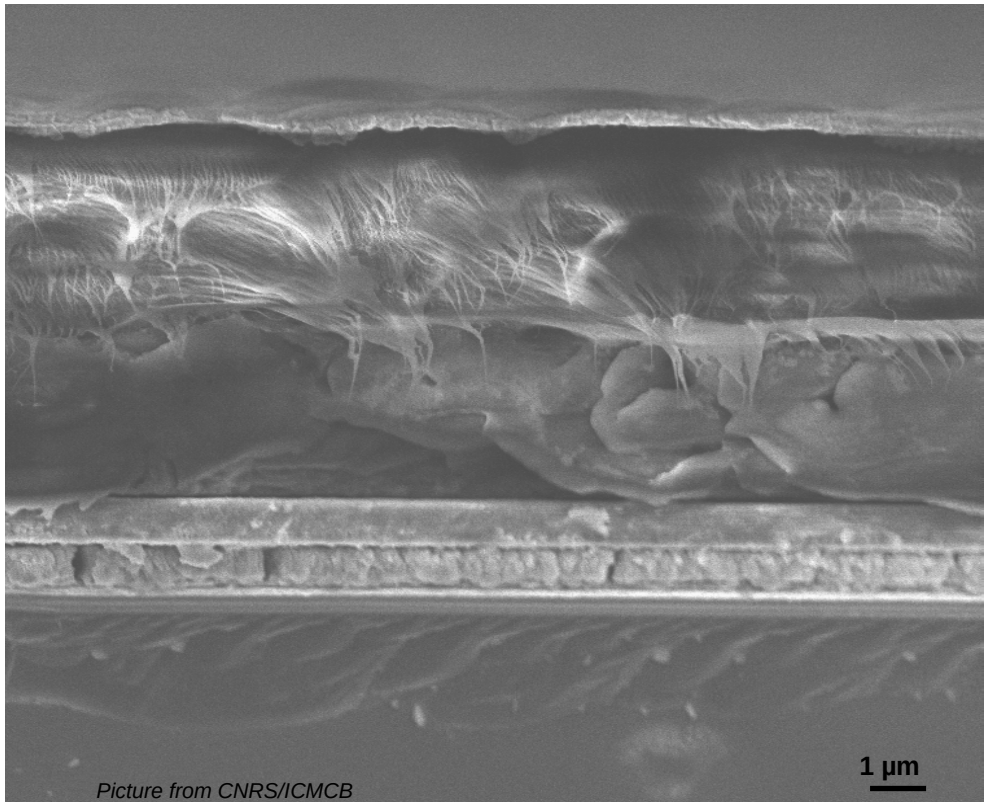


Microbattery SEM examination

Encapsulation

Active layers

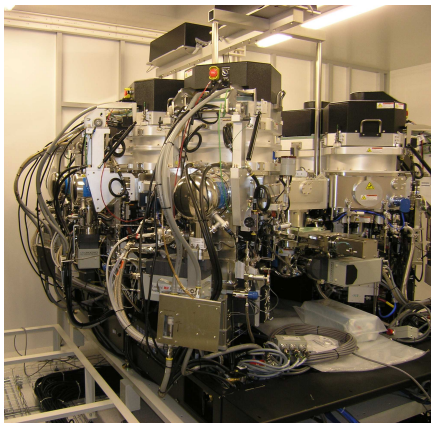
Substrate



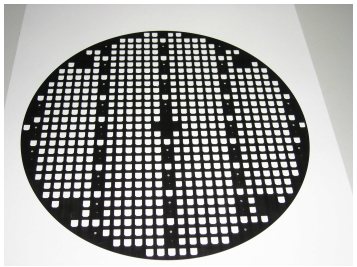
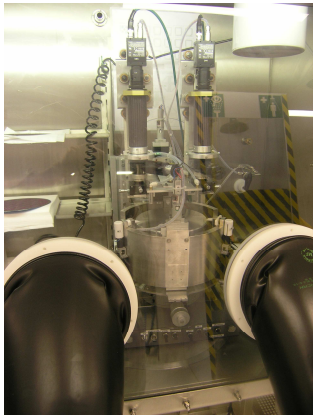
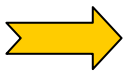
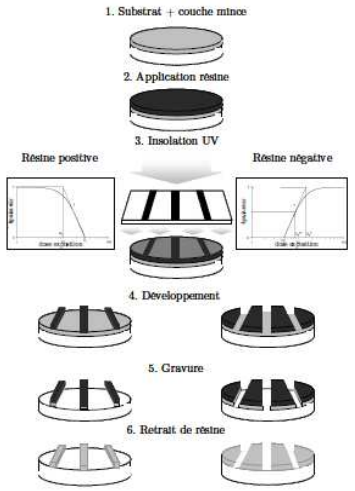
Picture from CNRS/ICMCB

Microbattery manufacturing

- **Process development on industrial tool (200mm substrates)**

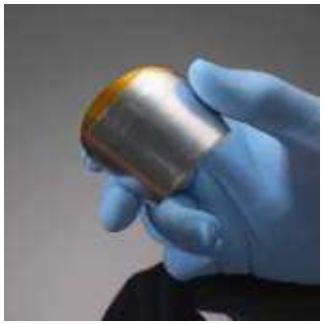


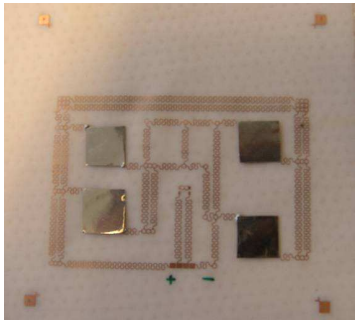

- **Patterning: from Shadow Mask to maskless process**

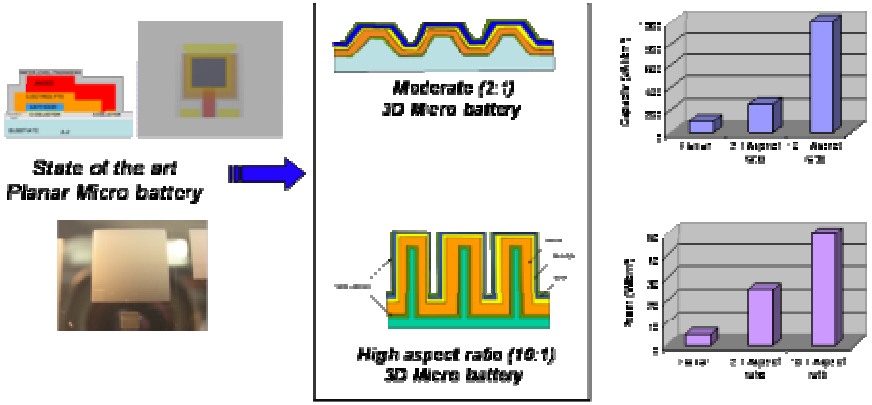
Substrates

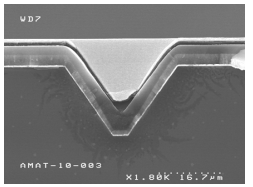
- **Flexible substrates**
  - Polyimide subtrates (low T process)
  - Large area for high capacity

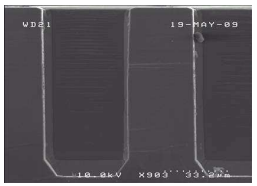




- **Textured substrates**







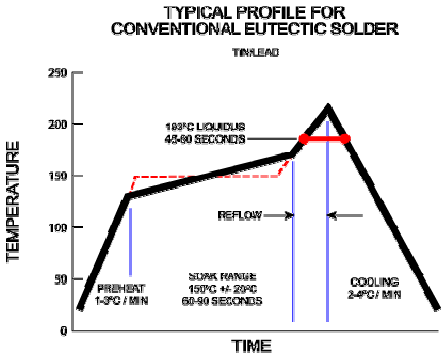
E-STARS

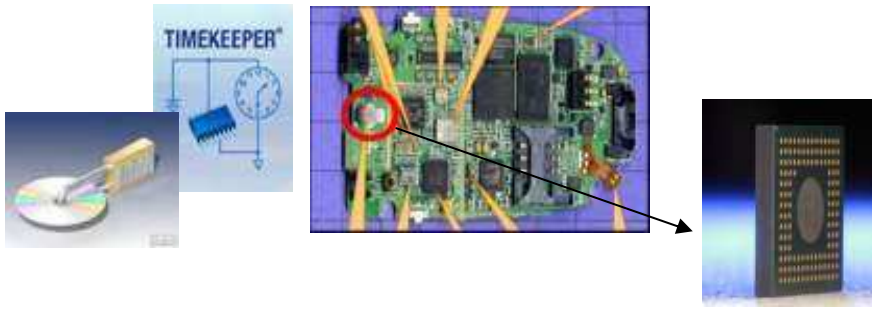
http://www.estars-project.eu

- **Stacking of microbatteries**

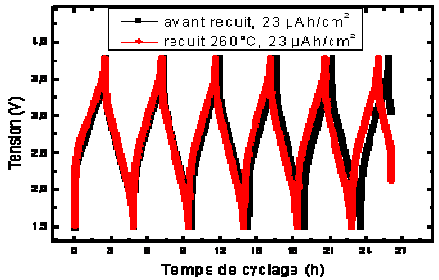
Integration: Solder reflow capability

- **Electronic market requires possibility to use energy storage as any other component**
  - Capability to sustain high temperature step for connection (SR)



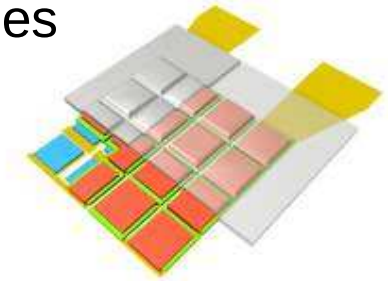


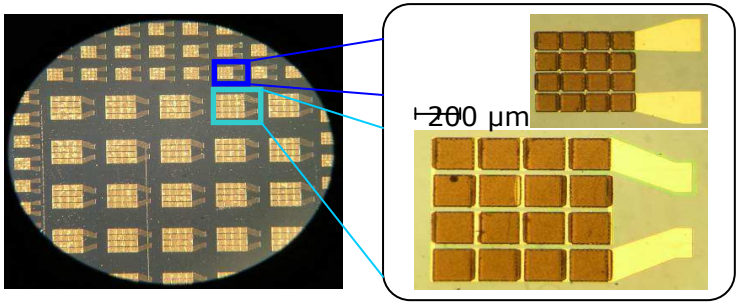
  - Microbattery Technology can fulfill the requirement
    - Microbattery cycling before and after 3 Lead free Solder Reflow

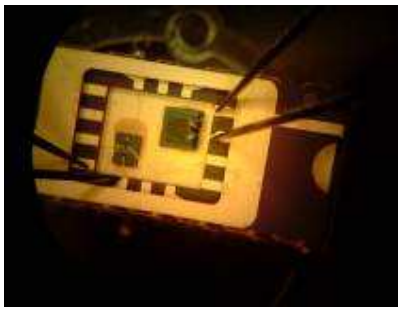


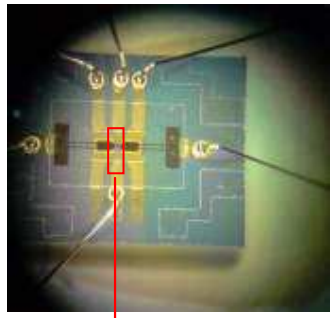
High voltage photolithography microbatteries

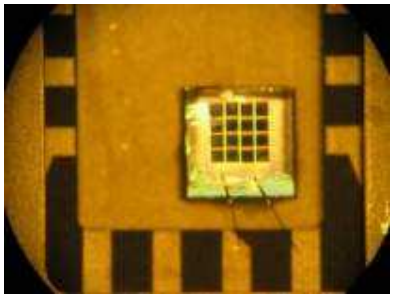
- **Objectives: High voltage (> 30V) energy source for rf MEMS**
  - Connections in series of 16 V_2O_5 based microbatteries
  - Photolithographic process
    - Standard clean room environment
    - 100 x 100 µm² microbatteries

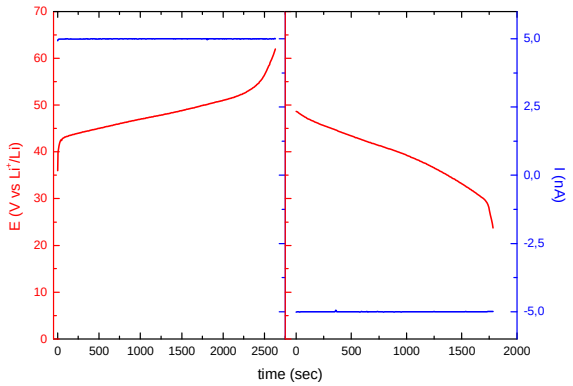






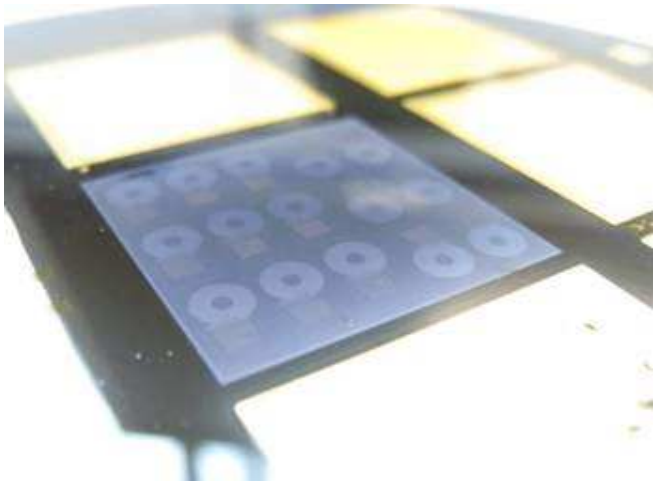


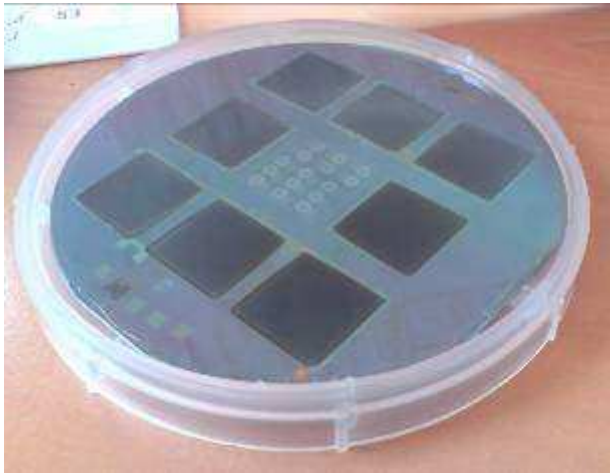




High voltage microbatteries

- **Objectives: High voltage energy source for actuators**
  - Technology fusion between silicon actuators and microbattery

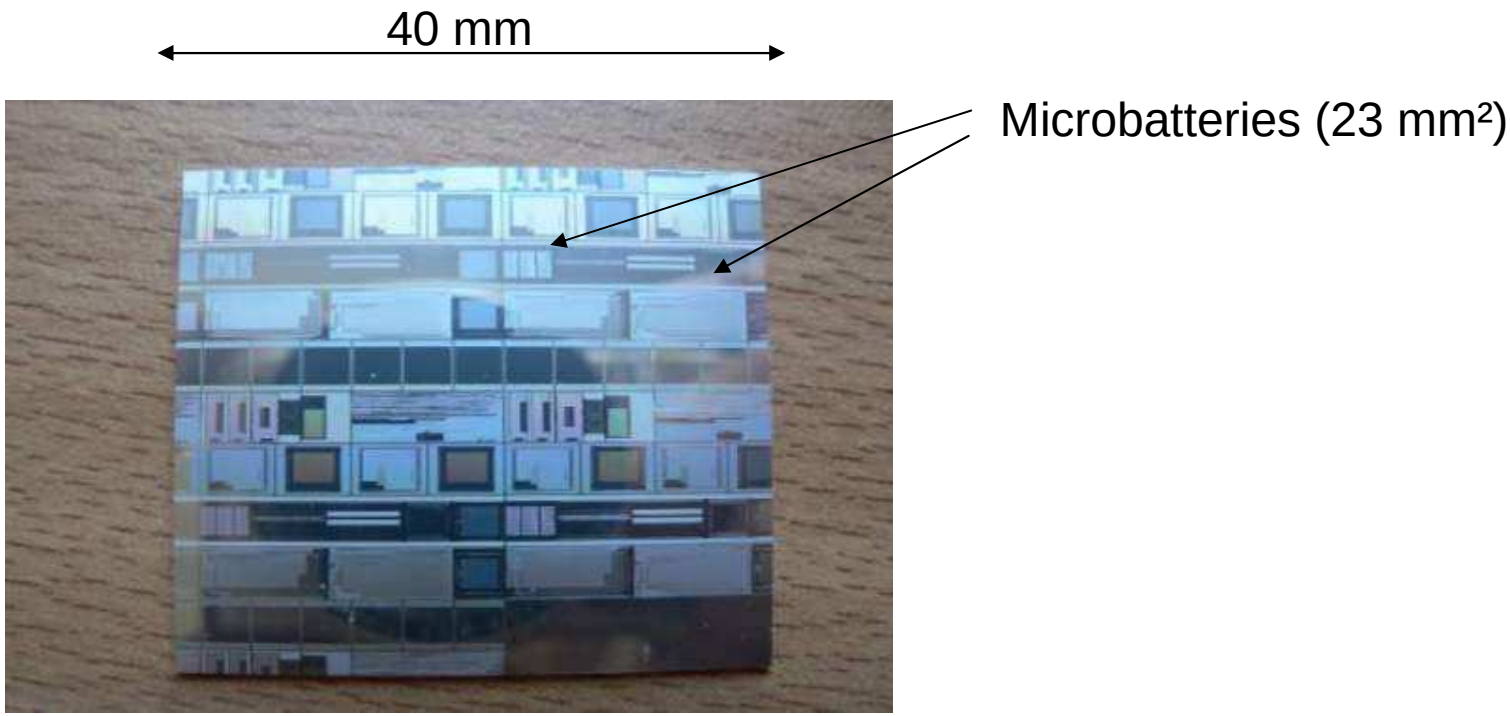




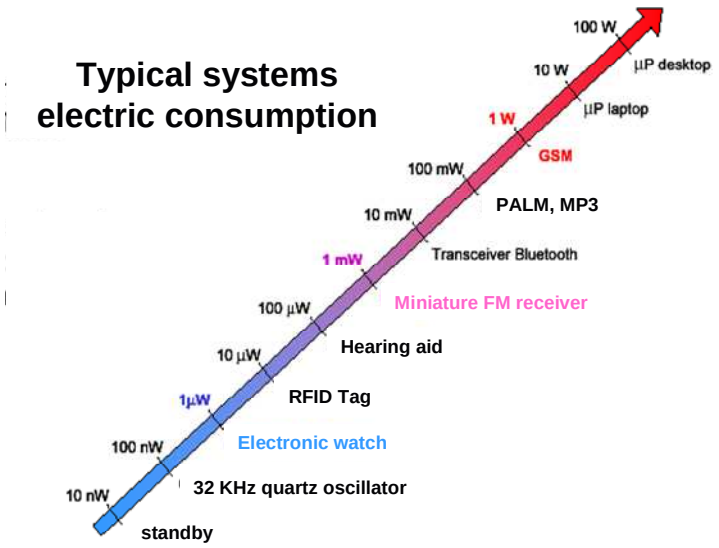
  - Applications: µUAV, avionics

Integration: Above IC capability

- Microbattery on integrated circuit for smart card application: security improvment



Autonomous micro-power system

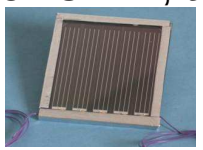


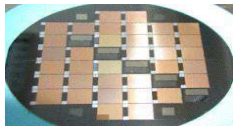
Micro-sensor's power

– Autonomous and long life time
– Miniaturization
– Integration

Hybrid micropower system: Storage + Harvesting

- **Microbateries are perfectly suited for these kind of requirements**
  - Thin film, integrable
  - High number of cycles w/o lose of capacity
  - Low self discharge
  - Pulse capabilities
  - Generic storage solutions for several energy harvesting systems: PV, thermoelectricity, piezo…

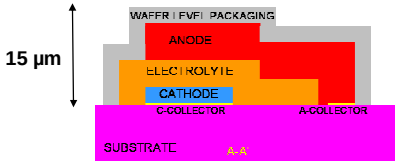


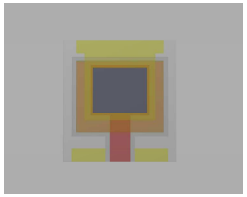


Microbattery Digest

	Available Microbatterie characteristics
Capacity	Up to 300 µAh/cm²
Power	Up to 3 mA/cm²
Voltage	Between 4.2 and 1 V
Cyclability	> Thousands of cycles
Thickness	< 15 µm (with packaging)
Surface	- From 20 mm² to large area (shadow mask) - Down to 100 x 100 µm (photolithography)
Substrate	IC (Si), polymer, ceramic, PCB…
Safety	Solid state – not flammable – no leakage

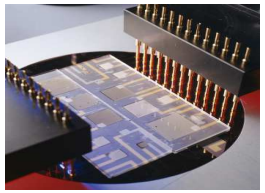
Evolution of CEA Microbatteries prototypes





First Integration of Microbatteries on IC

From 2 cm² to 25 mm² microbatteries (4'' wafer, Thick encapsulation)



2002

2004

2005

2006

2007

2008

2009

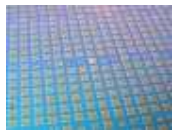
2010

2011

Microbatteries on 6'' wafers

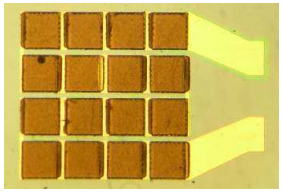
Microbatteries in 8x8 BGA package

Microbatteries on 8'' wafers

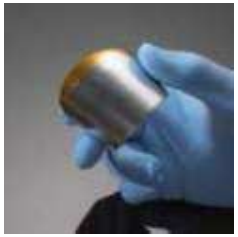


First Microbatteries Production line

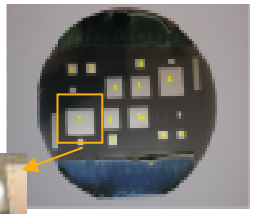
Microbatteries on 8'' wafers 5x5 LGA package



100 x 100 µm Microbatteries array for high voltage

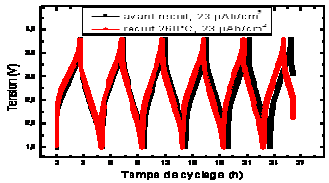


Microbatteries on flexible substrate



First microbatteries with thin film encapsulation (4'' wafer)

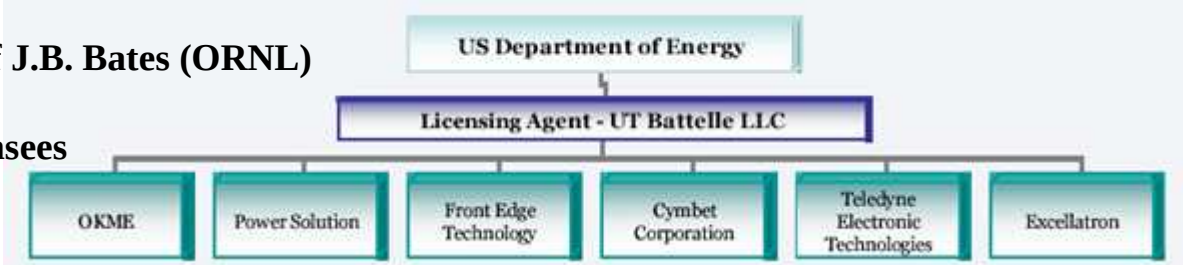
First Prototype (4'' wafer, Thick encapsulation)



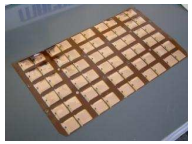
Microbatteries SR compatible

Industrial developments – US

All developments based on work of J.B. Bates (ORNL)
High temperature process
6 start-ups with non-exclusive licensees



➢ **Excellatron**
(Atlanta, Georgia)
www.excellatron.com



ATP-NIST program to develop PECVD process (speed-up the manufacturing process)
10.000 cells/month

➢**Cymbet**
(Elk River, Minnesota)
www.cymbet.com

2001: 4.5 M$ from 2 International venture capital firms
2004: 16.5 M$ from private financing (Dow Corning, Intel)
Project with Medtronics for medical applications
2009: microbatteries available for sale

➢**Infinite Power Solution**
(Denver, Collorado)
www.infinitepowersolutions.cc

Shareholding: UniSource Energy, Dow Corning
2006: raised 34.7 M$ for building microbattery building facilities
2008: raised 13 M$ for ramp-up

➢**Front Edge Technology**
(Baldin Park, California)
www.frontedgetechnology.com

50.000 prototypes
Testing contracts with Jet Prop. Lab
Small production line (200.000 pieces/year)

Industrial developments – Asia

➢ **Not a lot of public dissemination**

➢ **Nuricell** (Corea)
Start-up based on work performed at KIST
Owned by GS Caltex
Collaboration with Ulvac (equipment and target supplier)

➢ **Samsung** (Corea)
Known to work on the subject

➢ **Matsushita** (Japan)
Patenting

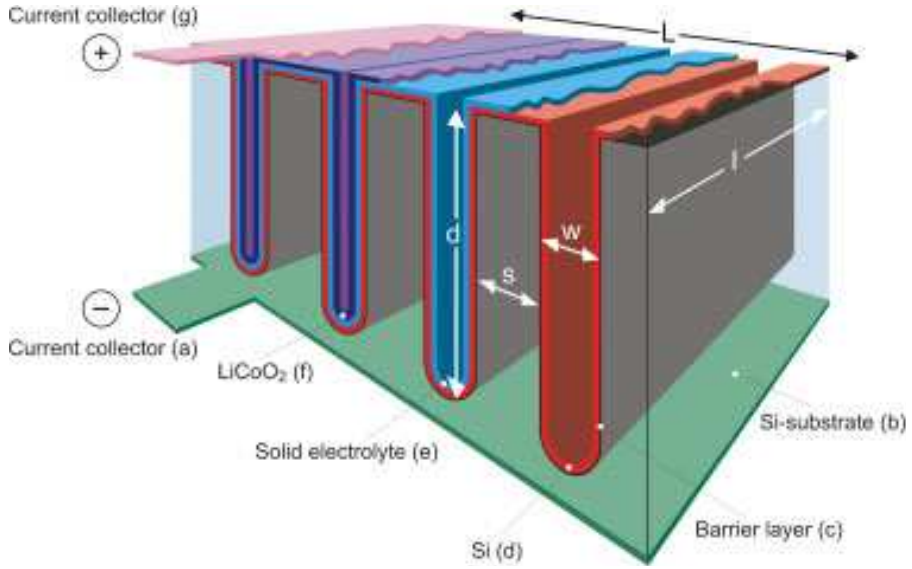
Positive electrode	Negative electrode	V1* (V)	V2** (V)	Ex.	Capacity maintenance ratio [%]	Capacity ratio [%]	Com. Ex.	Capacity maintenance ratio [%]	Capacity ratio [%]
$LiCoO_2$	C	4.2	3.0	2	85	88	2	55	46
$LiNiO_2$	C	4.2	3.0	3	75	77	3	45	43
$LiMn_2O_4$	C	4.2	3.0	4	81	85	4	36	34
$LiCoPO_4$	C	5.0	4.0	5	86	87	5	35	28
$LiFePO_4$	C	3.9	1.8	6	71	73	6	51	43
$LiCoPO_4F$	C	5.4	4.0	7	80	82	7	32	25
$LiFePO_4F$	C	3.9	1.8	8	79	79	8	41	29
$LiFeO_2$	C	4.1	1.5	9	77	77	9	51	31
$LiCoO_2$	Li	4.3	3.0	10	78	79	10	60	52
$LiNiO_2$	Li	4.3	3.0	11	72	75	11	44	39
$LiMn_2O_4$	Li	4.3	3.0	12	76	80	12	39	31
$LiCoPO_4$	Li	5.1	4.0	13	80	82	13	30	25
$LiFePO_4$	Li	4.0	1.8	14	71	75	14	45	31
$LiCoPO_4F$	Li	5.5	4.0	15	75	77	15	37	31
$LiFePO_4F$	Li	4.0	1.8	16	72	74	16	57	61
$LiFeO_2$	Li	4.2	1.5	17	69	72	17	59	58
V_2O_5	Li	3.6	1.5	18	85	89	18	60	34
$LiCoO_2$	Si	3.9	2.6	19	77	79	19	48	43
$LiNiO_2$	Si	3.9	2.6	20	71	74	20	47	40
$LiMn_2O_4$	Si	3.9	2.6	21	70	71	21	37	30
$LiCoPO_4$	Si	4.7	3.6	22	69	73	22	30	27
$LiFePO_4$	Si	3.6	1.4	23	75	77	23	49	42
$LiCoPO_4F$	Si	5.1	3.6	24	74	77	24	34	30
$LiFePO_4F$	Si	3.6	1.4	25	72	73	25	51	49
$LiFeO_2$	Si	3.8	1.1	26	69	73	26	45	40
$LiCoO_2$	$Li_4Ti_5O_{12}$	2.8	1.5	27	80	81	27	61	49
$LiNiO_2$	$Li_4Ti_5O_{12}$	2.8	1.5	28	75	79	28	57	49
$LiMn_2O_4$	$Li_4Ti_5O_{12}$	2.8	1.5	29	81	83	29	40	34
$LiCoPO_4$	$Li_4Ti_5O_{12}$	3.6	2.5	30	86	87	30	40	30
$LiFePO_4$	$Li_4Ti_5O_{12}$	2.5	0.3	31	71	73	31	47	39
$LiCoPO_4F$	$Li_4Ti_5O_{12}$	4.0	2.5	32	80	85	32	41	32
$LiFePO_4F$	$Li_4Ti_5O_{12}$	2.5	0.3	33	79	81	33	55	47
$LiFeO_2$	$Li_4Ti_5O_{12}$	2.7	0.0	34	77	78	34	52	44
V_2O_5	$LiCo_{2.5}O_{0.4}N$	3.1	1.0	35	88	88	35	46	37

V1*: end-of-charge voltage
V2**: end-of-discharge voltage

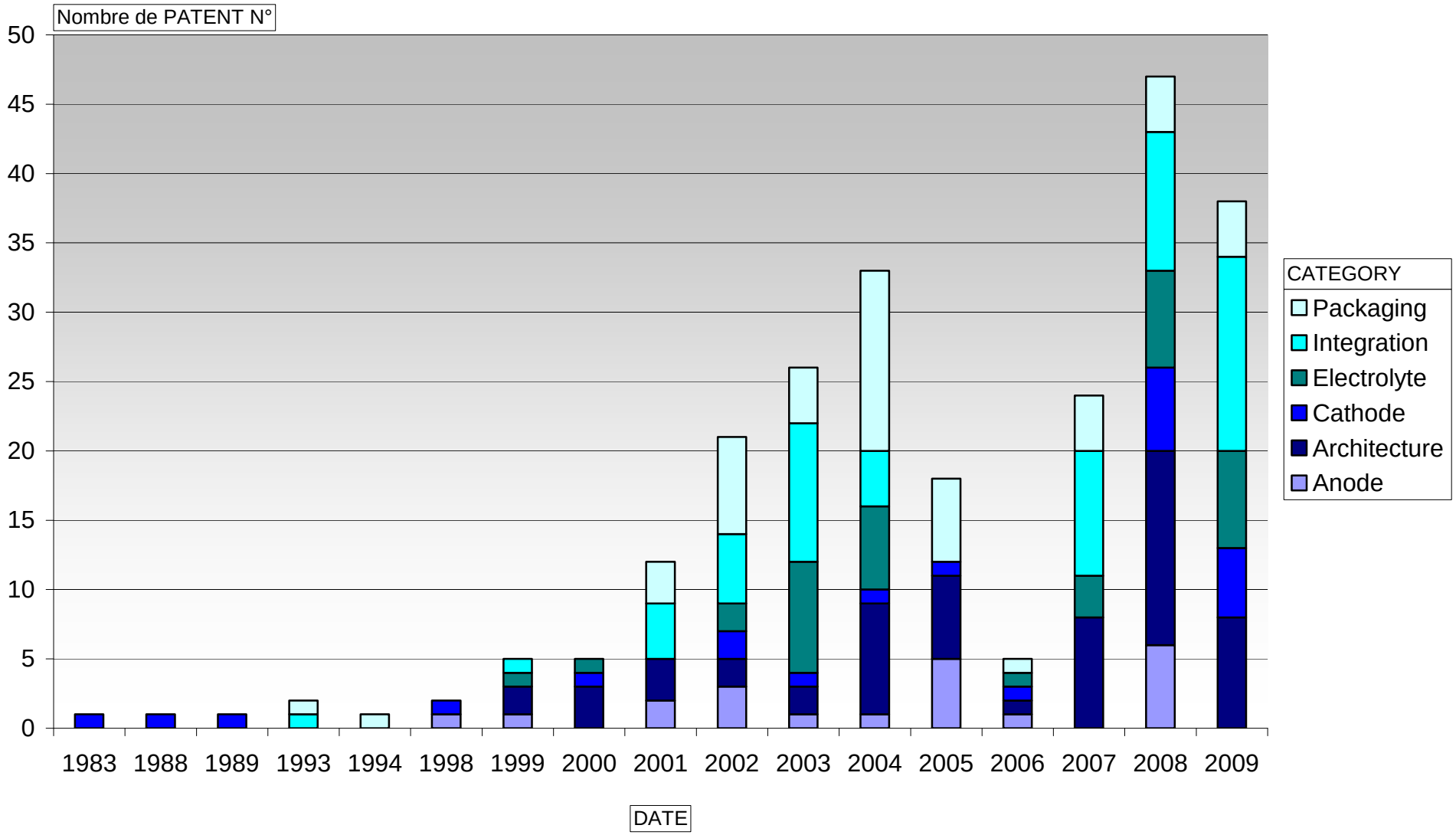
Industrial developments – Europe

➢ **ST-Microelectronics**
Common Lab with CEA-LITEN
Commercial agreement with Front Edge Technology (2009)

➢ **Philips Research**
Focused on 3D microbattery

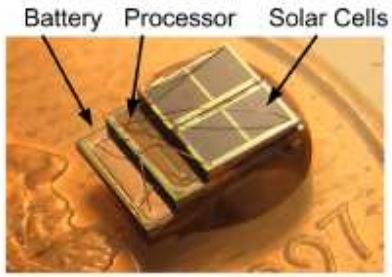


Evolution of microbattery patents in the world



Microbattery + energy harvesting prototypes

- **Microbattery + Photovoltaics**



- **Microbattery + RF**

- **Microbattery + Thermoelectricity**

Conclusions

- **Microbattery Technology**
  - Available with different packaging solutions
  - Solder Reflow compatibility for some of them
  - Industrialization on the road

- **Microsensors powering**
  - Hybrid system with energy harvesters
    - Depending on applications