Thin Film Solid State Batteries

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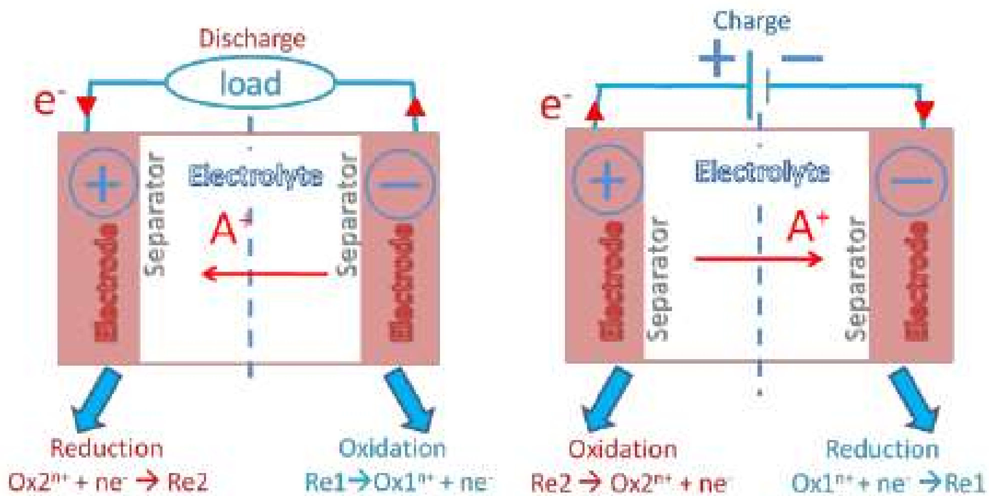
Outline

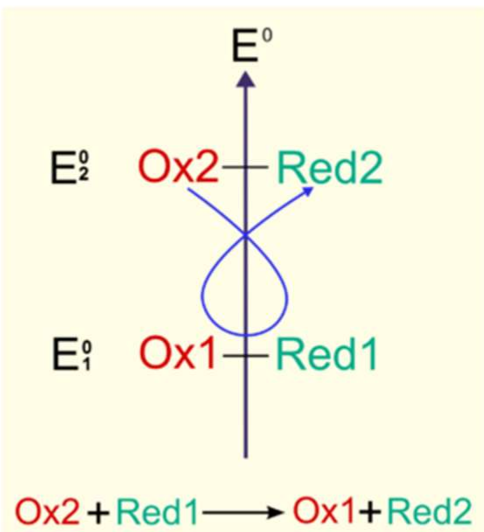
- Basics (lithium) of batteries
- Thin Film Solid State Batteries
  - Design, specific features and applications
  - Manufacturing process
  - Description conventional microbatteries
  - Examples of materials developments
  - Examples of particular designs

Basics of (lithium) batteries



Principle of an electrochemical generator

- Batteries are electrochemical cells in which the chemical energy is transformed into electrical energy.
- By using appropriate redox couple for each electrode the combination of the two half reaction is able to generate a spontaneous electron flow in the external circuit:



$$\Delta G = -nF(E_2 - E_1) < 0$$

$$E_2 > E_1$$

$$O_2 + R_1 \rightarrow R_2 + O_1$$

$$Cu^{2+} + 2e^- \leftrightarrow Cu$$

$$Zn^{2+} + 2e^- \leftrightarrow Zn$$

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu$$

Increasing reductive power

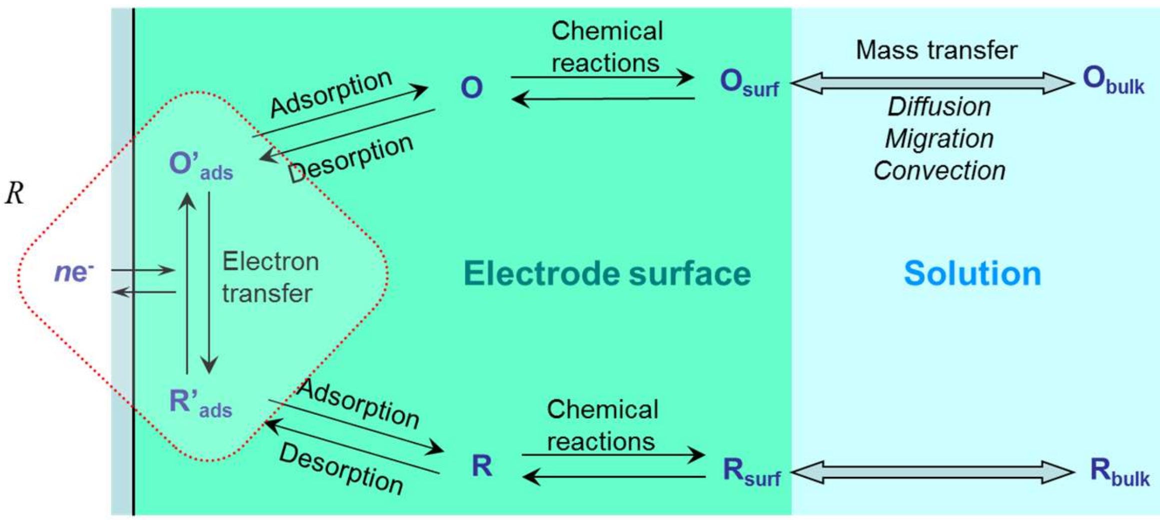
Couple redox	E^0 /ENH (V)
F_2/F^-	2.89
Ag^{2+}/Ag^+	1.989
Au^+/Au	1.69
$PbO_2,H^+/Pb^{2+}$	1.458
Cl_2/Cl^-	1.296
$O_2,H^+/H_2O$	1.229
Pt^{2+}/Pt	1.180
Pd^{2+}/Pd	0.915
Ag^+/Ag	0.799
Hg^{2+}/Hg	0.648
Cu^{2+}/Cu	0.439
$N_2,H^+/NH^{4+}$	0.274
H^+/H_2	0.000
$GeO_2,H^+/Ge$	-0.104
Pb^{2+}/Pb	-0.126
Sn^{2+}/Sn	-0.141
Ni^{2+}/Ni	-0,260
Co^{2+}/Co	-0.280
Cd^{2+}/Cd	-0.402
Cr^{3+}/Cr	-0,74
Zn^{2+}/Zn	-0.760
$SiO_2,H^+/Si$	-0.990
Ti^{3+}/Ti	-1.370
Zr^{4+}/Zr	-1.450
Al^{3+}/Al	-1.677
Be^{2+}/Be	-1.968
Mg^{2+}/Mg	-2.360
Na^+/Na	-2.714
Ca^{2+}/Ca	-2.868
K^+/K	-2.936
Li^+/Li	-3.040

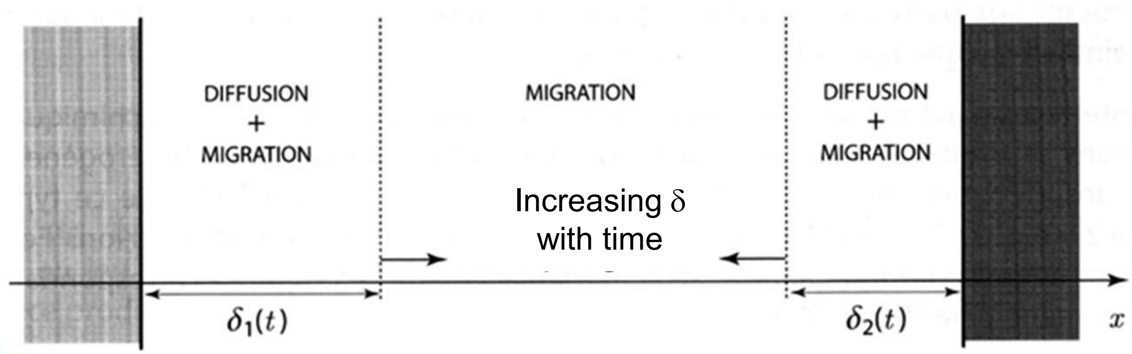
Increasing oxidative power

Principle of an electrochemical generator

- The amount of electrons that is delivered is proportional to the amount of oxidized/reduced materials (Faraday's law)
- Contrary to electronic devices, the operation of electrochemical cell involves **both electronic and ionic transport**, that are correlated.
- Mass transport is often a limiting step for battery operation

$$O + ne^{-} \rightarrow R$$



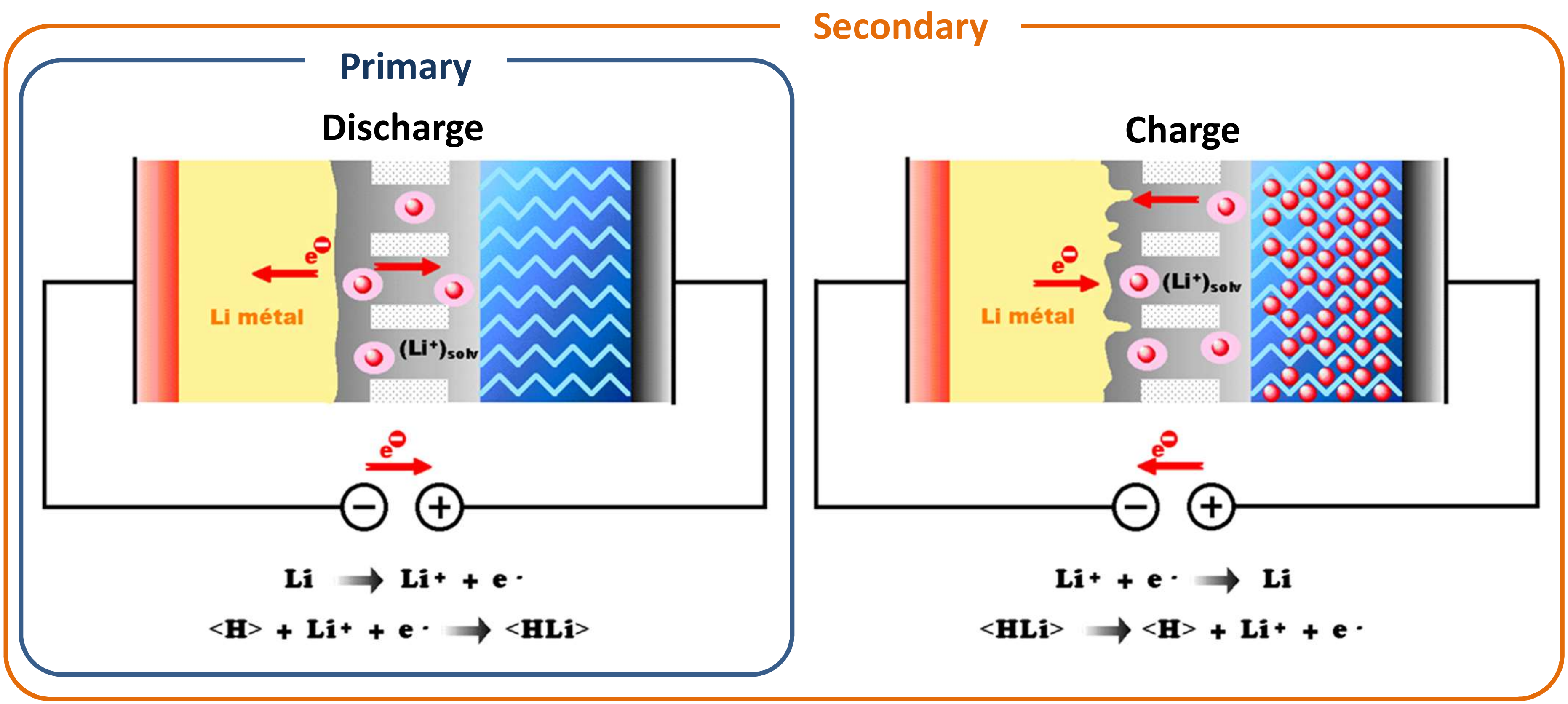


Battery features

- **Main features of an electrochemical energy storage device (battery)**
  - Capacity (Coulomb or A.h) $\propto$ amount of electrode material
  - Cell voltage (V)
  - **Energy density (W.h/kg and Wh/l)**
  - Power density (W/kg, W/l)
  - Internal resistance / Impedance (Ω)
  - Calendar life
  - **Cycle life (secondary batteries)**
  - Coulombic/ Energy efficiency (secondary batteries)
  - Self-discharge rate
  - **Cost**
  - **Safety**
  - Environmental footprint (raw materials, manufacturing process, recycleability)

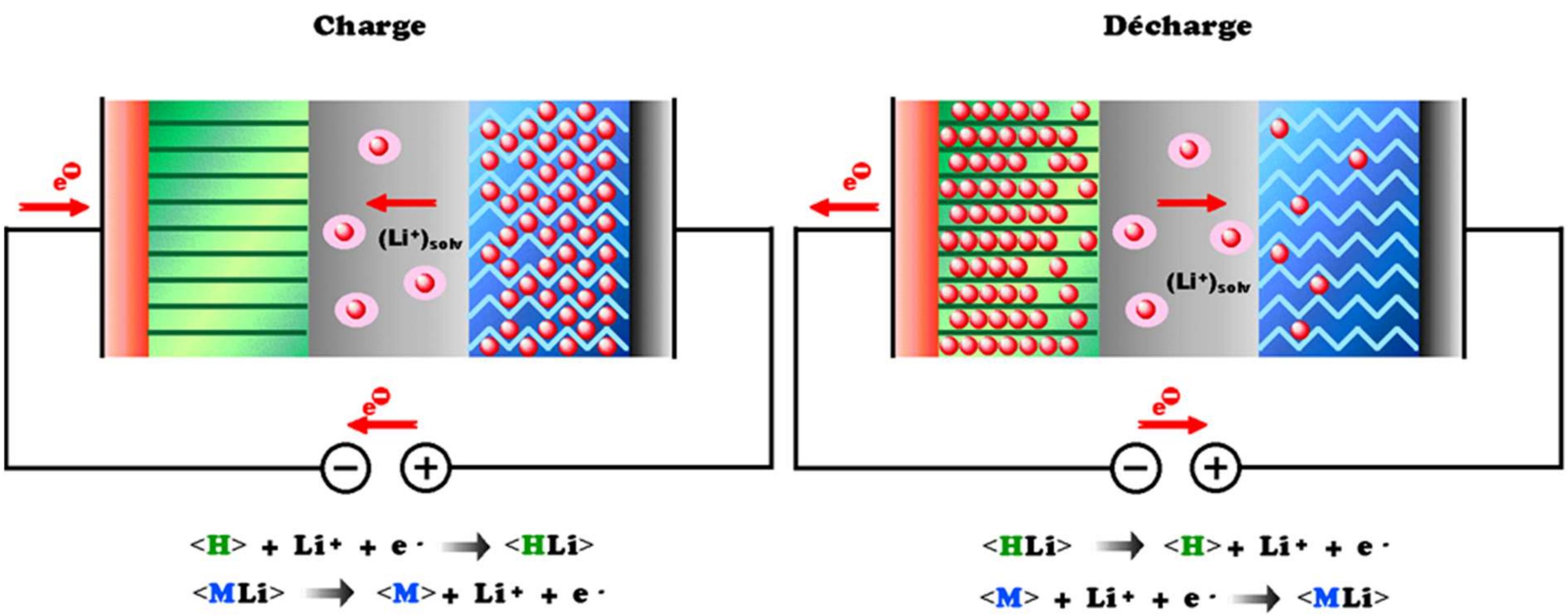
Lithium batteries

- **Particular interest of Li batteries**
  - Lithium has the lowest redox potential (-3.05 V/HNE)
  - Using a Li metal negative electrode allows to built cells with higher e.m.f (3-4 V) compared to aqueous cells (1.2-1.5 V) ⇨ high energy density
  - Requires the use of aprotic solvents for the liquid electrolyte



Lithium-ion batteries

- **Rechargeable batteries using two intercalation materials**
  - Lithium metal is replaced by a layered material (Graphite) that react at low voltage with Li^+ according to an intercalation process to form LiC_6.
  - Improvement of operation safety, while keeping a high energy density
  - The positive electrode is an intercalation material (2D, 3D or 1D channel network), generally a lithiated transition metal oxide.



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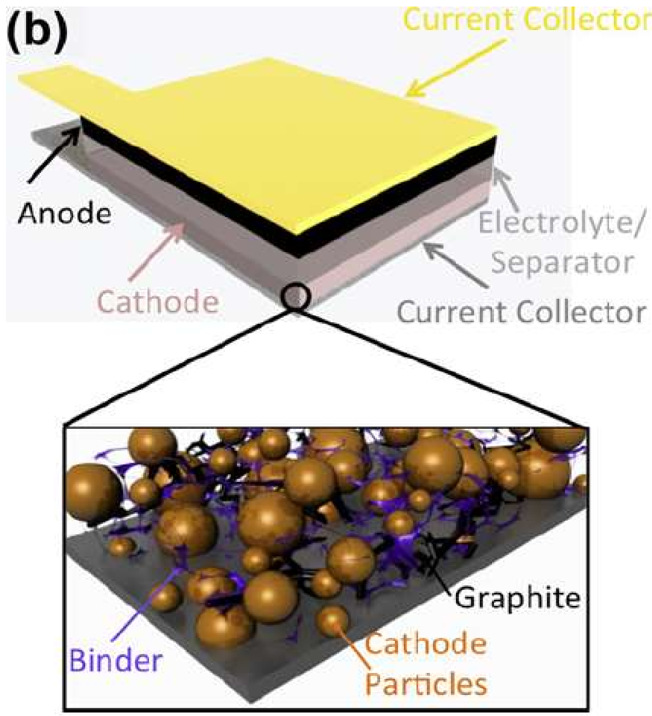
  - Principle of Li-ion cells proposed by W. Murphy (1975)
  - Commercialized by Sony - Asahi Kasei (1991) on the basis of :
    - Layered oxide $LiCoO_2$ (J.B. Goodenough 1980)
    - Graphite (Reversible intercalation of Li, R. Yazami 1983)
    - Practical cell developments (A. Yoshino, 1985)

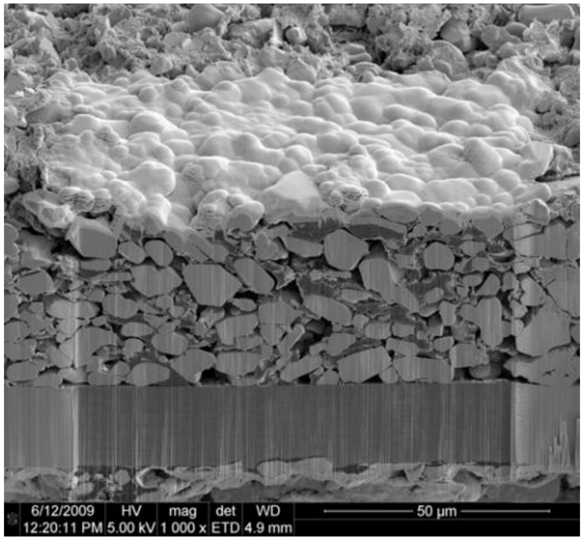
+ $LiCoO_2 \leftrightarrows xLi^+ + xe^- + Li_{1-x}CoO_2$ E+ ~ 3,7-4,2 V/Li+/Li

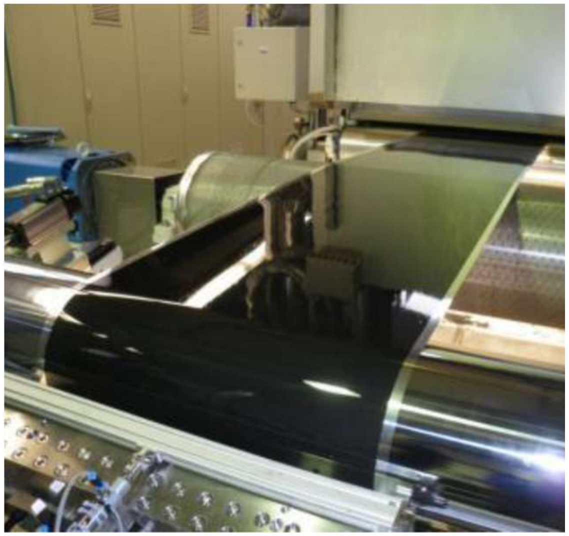
- $6\,C + Li^+ + e^- \leftrightarrows LiC_6$ E- ~ 0,08-0,25 V/Li+/Li

Lithium-ion batteries

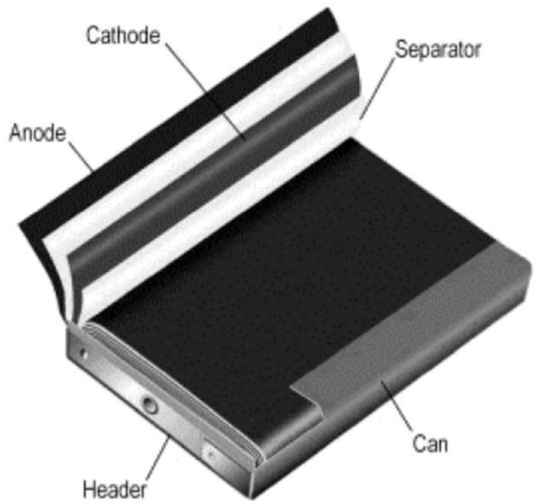
- **Typical structure of a Li-ion battery**
  - Positive electrode: Active material (92-95 wt% + carbon additive (3-5 wt%) + polymer binder (PVdF) coated on an Al foil
  - Negative electrode: Graphite or coke (>90 wt%) + carbon additive (3-5 wt%) + binder (PVdF or CMC) coated on a Cu foil
  - Electrolyte: liquid electrolyte composed of organic solvent and a Li salt (LiPF6) impregnated in the porous electrodes. Separator: microporous polyolefine membrane or gelled electrolyte membrane ('Li-polymer').

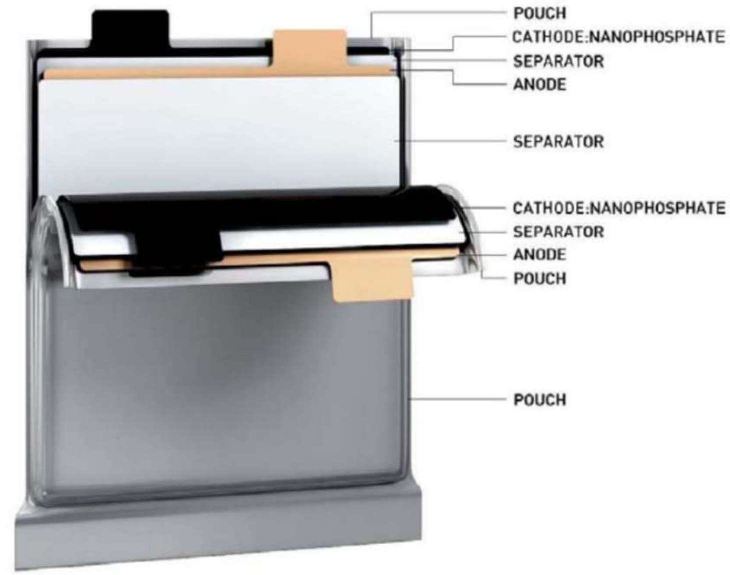






- **3 main formats of Li-ion batteries**



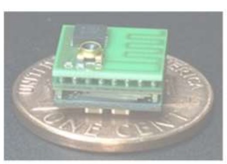


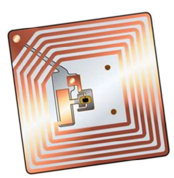
Cylindrical	Prismatic	'Li polymer'
Liquid electrolyte Rigid casing	Liquid electrolyte Rigid casing	Gel electrolyte Soft packaging (pouch)

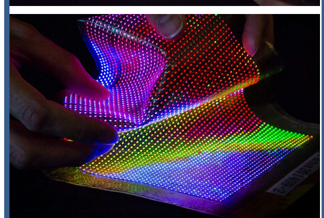
Batteries: Energy storage systems at various scales

IoT, MEMS, CMOS memories, Medical implantable	Smart cards, Skin patch, RFID	Wearables, E-textile, Medical device	Smartphone, Tablet, Power tool, Toy	Transport	Large-scale energy storage
Capacity range					
1 mAh	10 mAh	100 mAh	1 Ah	100 Ah	> 1kAh
Energy range					
1 mWh	10 mWh	1 Wh	10 Wh	1-100 kWh	> 1MWh
• Rechargeable • Small footprint (microbatteries) • Long life • Fast discharge • Te[illegible] incorporate with energy harvesting	• Can be both disposable and rechargeable • Laminar and thin, some with special form factor • Relatively low power • Cost sensitive	• High energy density for small volume • Long working hours • Flexible, stretchable or thin, some with special form factor	• Light-weight and small volume • Long working hours, Some special form factors • High power	• Safe • Reliable • High power • High energy density • Cost per KWh	Long life time Reliable High capacity Cost per cumulated KWh

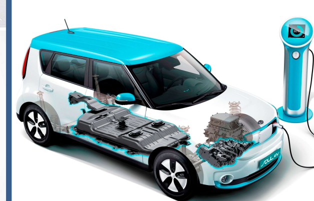
All solid-state micro-Batteries



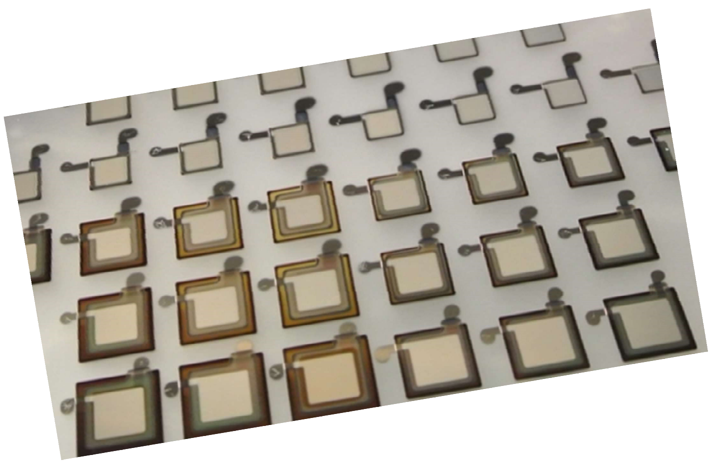





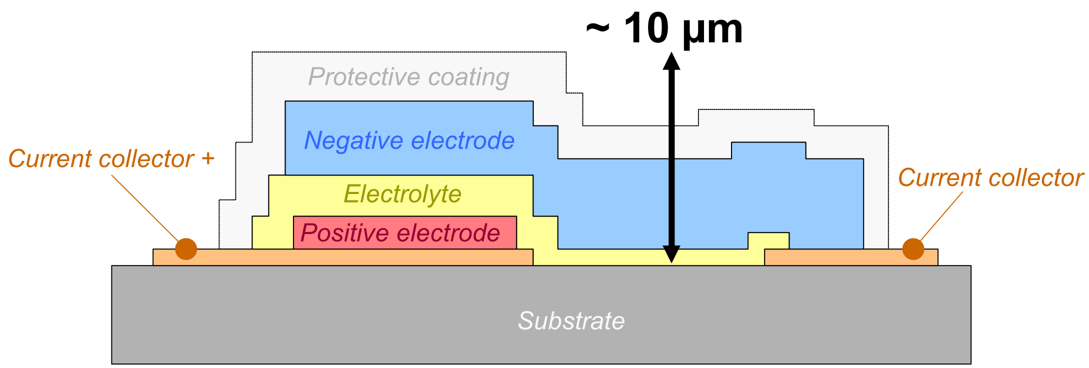



All-solid-state Microbatteries

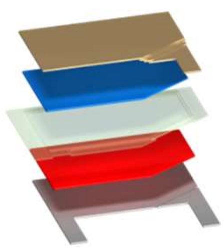


What is an all-solid-state lithium microbattery ?



- Stack of thin solid films obtained by vacuum deposition techniques

Si wafer, glass, mica, polyimide, PET, metal foils → Pt, Ni, W, Ti,… → V_2O_5, TiOS, $LiCoO_2$, $LiMn_2O_4$,… → LiPON, LiBSO → Li metal, Si, Ge, Sn, …, SnO_x → Pt, Ni, W, Ti,… → Multil-layer coating, Polymer, SiO_x, Al_2O_3



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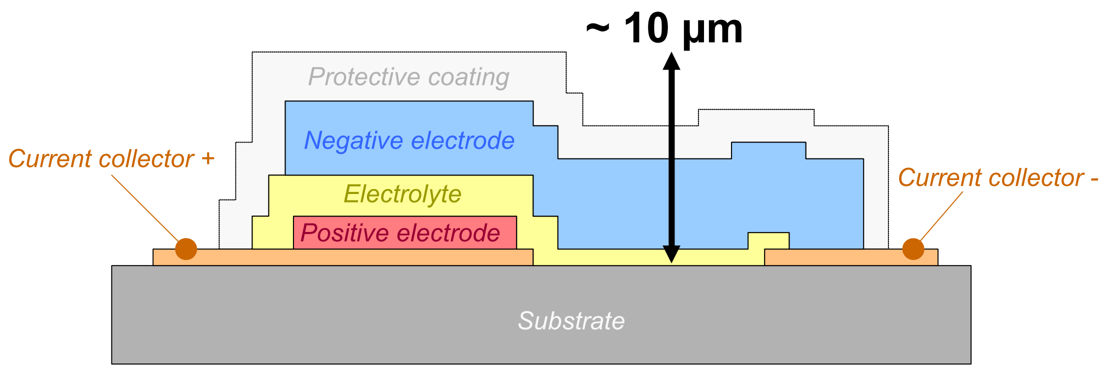
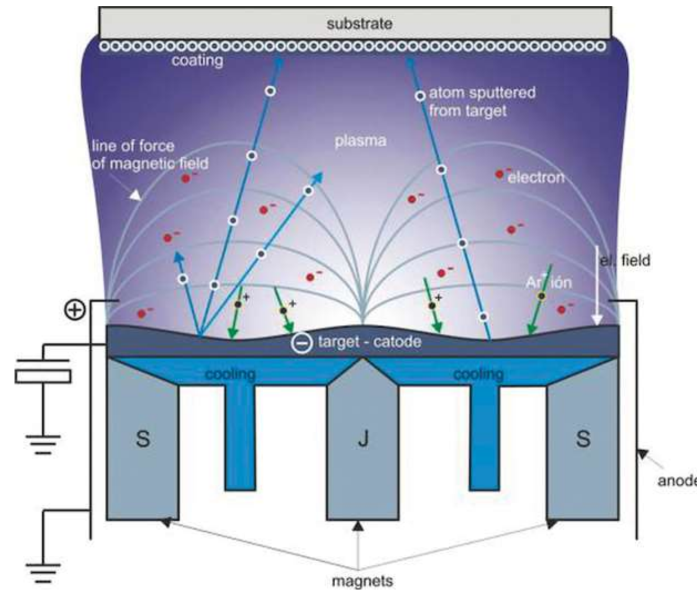


- Stack of thin solid films obtained by vacuum deposition techniques
- Performance
  - Capacity ~ 200-600 µAh.cm^{-2}
  - High cycle life (1k-10k cycles), calendar life (~10y), possibly high voltage (~5V)
  - Low self discharge (<5%/year)
  - Sustain high temperature (operation, storage)
- Distinctive features
  - Reduced footprint and/or thickness of the whole cell
  - Additive assembly process - Monolithic structure
  - Cost of raw material (targets) ≪ total manufacturing cost
  - Specific capacity (mAh.g^{-1}) criterion not relevant

⇨ Selected active materials ≠ Conventional Li-ion batteries

Thin film deposition by sputtering

- Process widely used in the microelectronics industry
- Suitable for 'simple' chemical compositions
- Preparation of new materials, possibly metastable using various modes:
  - DC or RF
  - Reactive sputtering
  - Co-sputtering
  - Multi-layers
- Deposition rate of oxides in the range 0.1 to 0.5 $\mu m.h^{-1}$
- Cost of the film: processing time ≫ cost of raw materials



- ✓ Power
- ✓ Total pressure
- ✓ Target-substrate distance
- ✓ Oxygen partial pressure
- ✓ Substrate polarization (bias)
- ✓ Type of substrate
- ✓ Substrate Temperature
- ✓ …

- ✓ Composition
- ✓ Structure
- ✓ Morphology
- ✓ Deposition rate

- ✓ Electrochemical behavior

Historical milestones

1983 **TiS_2 or TiOS as positive electrode**

Kanehori et al. (Hitachi) — TiS_2 (CVD, PECVD)/LISIPO/Li [1]

Levasseur et al. (ICMCB, Bordeaux) — $TiOS/Li_2SO_4\text{-}Li_2O\text{-}B_2O_3/Li$ [2]

Akridge et al. (Eveready Battery Company) — $TiS_2/LiI\text{-}Li_3PO_4\text{-}P_2S_5/Li$ [3]

1992 **Discovery of a new electrolyte: LiPON**

Bates et al. (Oak Ridge National Lab) [4], used in commercial microbatteries

1996 **1st use of $LiCoO_2$ as positive electrode**

Bates et al., various combinations of positive electrodes ($LiCoO_2$, $LiMn_2O_4$, V_2O_5) and negative ones (Li, SiTON, Zn_3N_2, Sn_3N_4) [5]

2000 **« Li-free » microbattery manufactured without Li metal**

Neudecker et al., Li is electrodeposited on the current collector during the charge

2001 **Emergence of Li-ion microbatteries**

2004 **Development of new deposition processes** (sol-gel, ink-jet, laser) and novel **3D architectures**

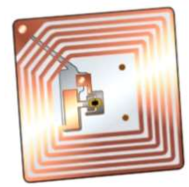
[1] K. Kanehori et al., *Solid State Ionics*, 18-19 (1986) 818; [2] G. Meunier, R. Dormoy, A. Levasseur, patent WO9005387 (1988); [3] S. D. Jones, J. R. Akridge, *Solid State Ionics*, 53-56 (1992) 628; [4] J. B. Bates et al., *Solid State Ionics*, 53-56 (1992) 647; [5] J. B. Bates et al., *J. Electrochem. Soc*. 147(2) (2000) 517

Applications

- Energy back up for portable electronics
  - Real-time clocks
  - DRAM, SRAM

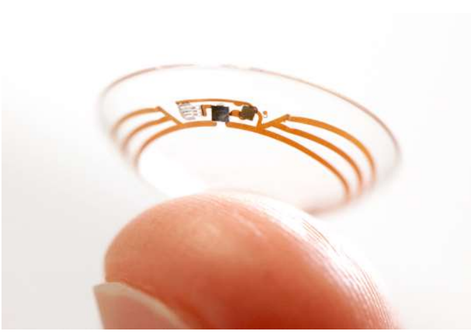
- Secured Pay Cards

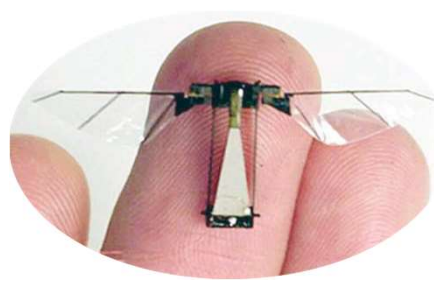
- Battery-assisted Passive and Active RFID tags

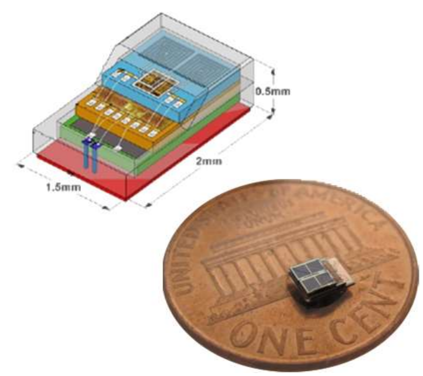


- Systems-in-Package components (SiP)

- Low consumption sensors and actuators (+ energy harvesting devices): medical devices, wearable devices, smart packaging, …







Typical industrial manufacturing process

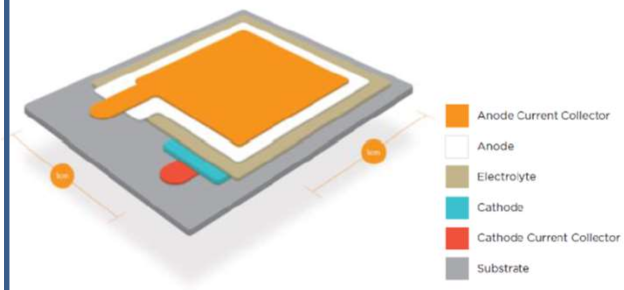
Present (and past) industrial products

IPS Thinergy MEC101

- 4,0 V Li-metal cell
- 25,7 x 25,7 mm² , 170 µm thick – 450 mg
- 1000 µAh
- 150 µAh.cm⁻²
- Peak current: 50 mA max

STMicro EFL700

- 4,0 V Li-metal cell
- 25,7 x 25,7 mm²
- 1000 µAh
- 150 µAh.cm⁻²
- Peak current: 10 mA / 100 ms

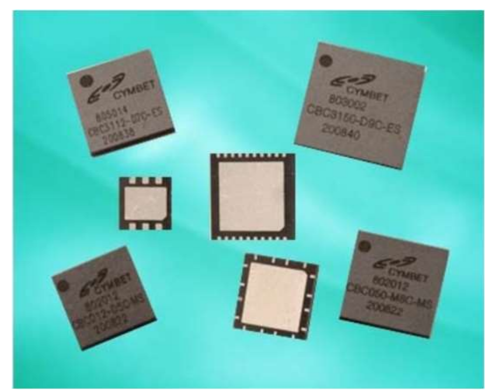


Ilika Stearax M250

- 3.5 V Li-ion cell
- 10 x 10 mm², 750 µm thick – 270 mg
- 250 µAh
- 250 µAh.cm⁻²
- Peak current: 5 mA / 500 ms

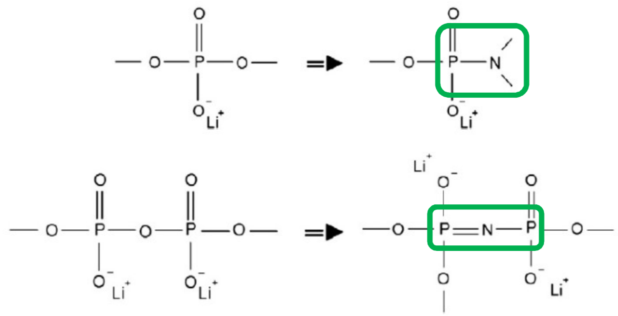
Cymbet EnerChip CBC012

- 4,0 V 'Li-free' cell
- 5 x 5 mm² , 900 µm thick
- 12 µAh
- 50 µAh.cm⁻²
- Lead-free reflow tolerant

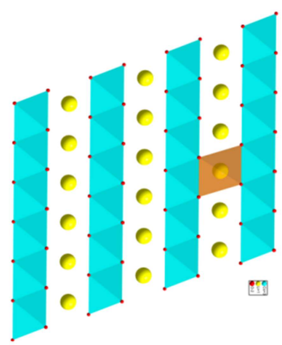


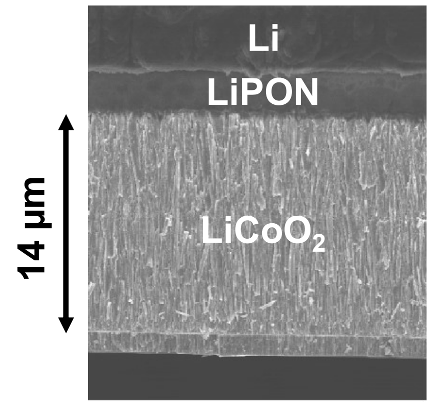
Li – LiPON – $LiCoO_2$: a triptych becoming a standard

- First Li-LiPON-$LiCoO_2$ cell by J. Bates *et al.* (1996) [1]
  - Then adopted by Front Edge Technologies, Cymbet, IPS, ST Microelectronics, GS Nanotech…
- LiPON (lithium phosphorus oxynitride) [2]
  - RF sputtering of a Li_3PO_4 target, in a pure N_2 atmosphere
  - Glassy material ➡ good mechanical properties
  - Chemically stable vs Li metal
  - Ionic conductivity at RT: 3.10^{-6} $S.cm^{-1}$ ($Li_{3.2}PO_{3.0}N_{1.0}$) [3]
  - ‘Stable’ up to 5 V/Li^+/Li



- Li metal
  - Deposition by evaporation or sputtering
  - No dendrites with a solid electrolyte
- $LiCoO_2$ layered oxide
  - Volume capacity: 69 $\mu Ah.cm^{-2}.\mu m^{-1}$
  - Mean discharge voltage ~ 4 V/Li^+/Li
  - High cycle life between 3.0-4.2 V/Li^+/Li
  - Facile Li diffusion between CoO_2 slabs
  - Metal-type electronic conductivity in $Li_{1-\varepsilon}CoO_2$ [4]





[5]

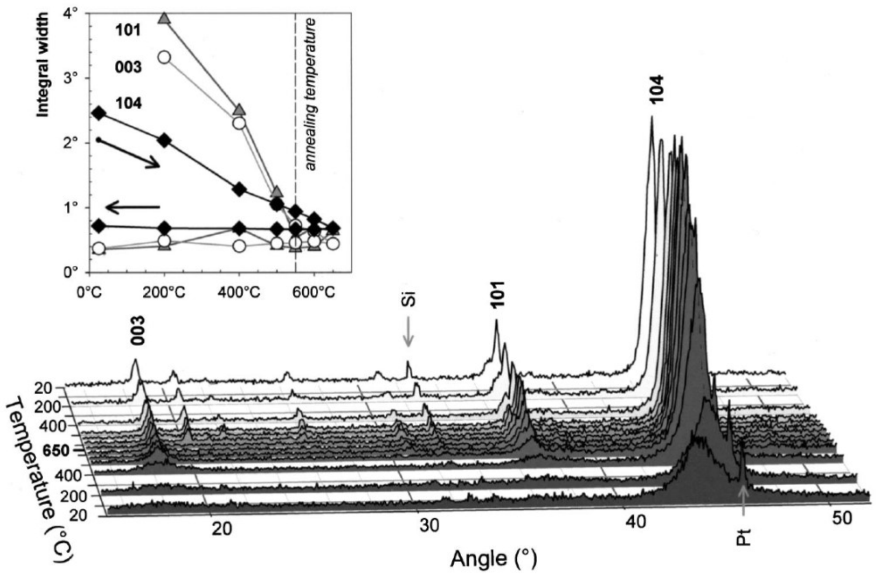
Thicker electrodes - Higher surface capacity

[1] B. Wang, J.B. Bates, F.X. Hart, B.C. Sales, R.A. Zuhr, J.D. Robertson, *J. Electrochem. Soc.*, 143, 3203- (1996)
[2] J.B. Bates, N.J. Dudney, G.R. Gruzalski, R.A. Zuhr, A. Choudhury, C.F. Luck, J.D. Robertson, *J. Power Sources*, 43, 103-110 (1993)
[3] B. Fleutot, B. Pecquenard, H. Martinez, M. Letellier, A. Levasseur, Solid State Ionics,
[4] J. Molenda, A. Stokłosa, T. Bąk, *Solid State Ionics*, 36, 53-58 (1989) [5] S. Nieh – Front Edge Technologies, *NEST Workshop, Lyon, France* (2009)

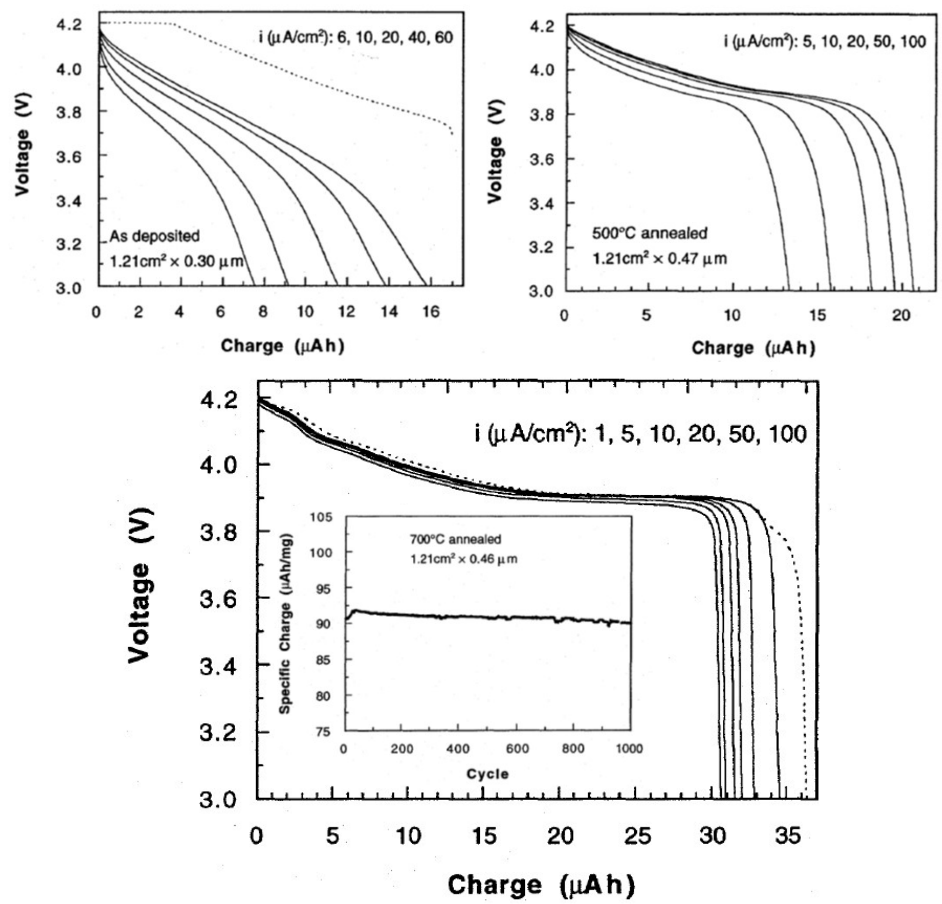
Specifity of the $LiCoO_2$ thin film electrode

- Post deposition annealing is required to obtained the ordered *R-3m* layered oxide
  - As-deposited $LiCoO_x$ is amorphous
  - Annealing in air/oxygen required at 550 – 650°C
  - Thermo-mechanical, thermo-chemical compatibility with the substrate

  ⇨ Pt, Au, Ni current collectors



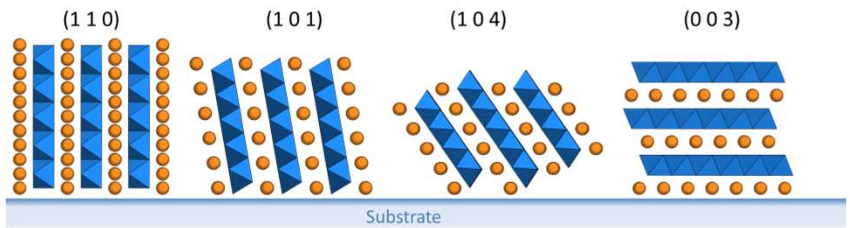
P. J. Bouwman, B. A. Boukamp, H. J. M. Bouwmeester, P. H. L. Notten
J. Electrochem. Soc., 149, A699-A709 (2002)



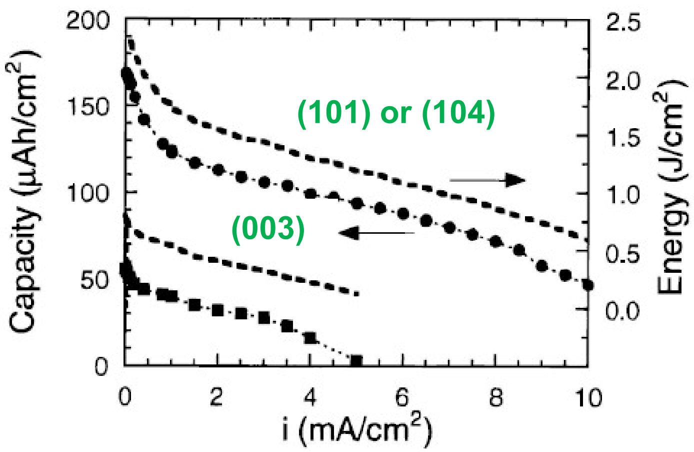
B. Wang, J.B. Bates, C.F. Luck, B. C. Sales, R. A. Zuhr, amd J. D. Robertson,
in 'Thin -Film Solid Ionic Devices and Materials', ed. by J.B. Bates, Electrochemical Society (1996)

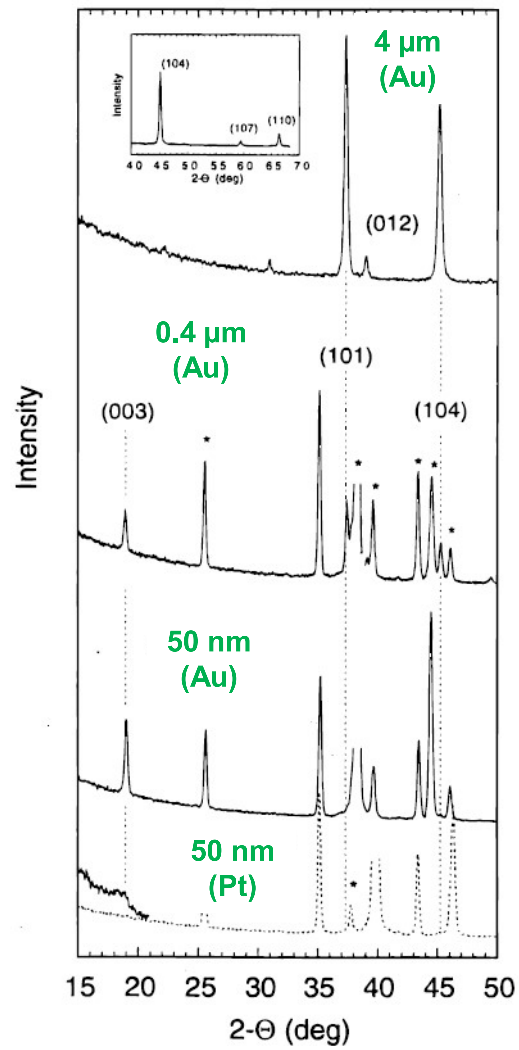
Specifity of the $LiCoO_2$ thin film electrode

- The preferred orientation of the $LiCoO_2$ film has to be monitored [1,2]



- Layered material ➡ anisotropic Li^+ diffusion
- (0 0 3) preferred orientation to be avoided
- Substrate dependent
- May vary with the thickness of the film





[1] J. B. Bates, N. J. Dudney, B.J. Neudecker, F.X. Hart, H.P. Jun, S.A. Hackney, *J. Electrochem. Soc.*, 147, 59-70 (2000)
[2] Y. Yoon, C. Park, J. Kim, D. Shin, *J. Power Sources*, 226, 186-190 (2013)

Systems beyond Li/LiPON/$LiCoO_2$

- New material optimized solutions for generic needs:

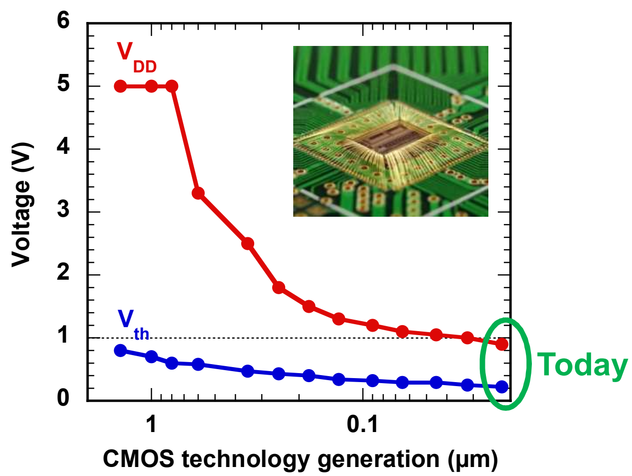
  Improved capacity per surface/volume unit

Systems beyond $Li/LiPON/LiCoO_2$

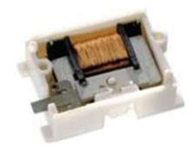
- New material optimized solutions for generic needs:

Improved capacity per surface/volume unit

Lower operating voltages

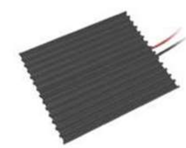


Motion



Solar

Thermo

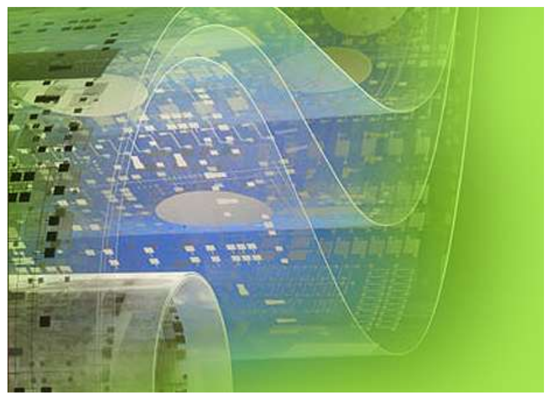


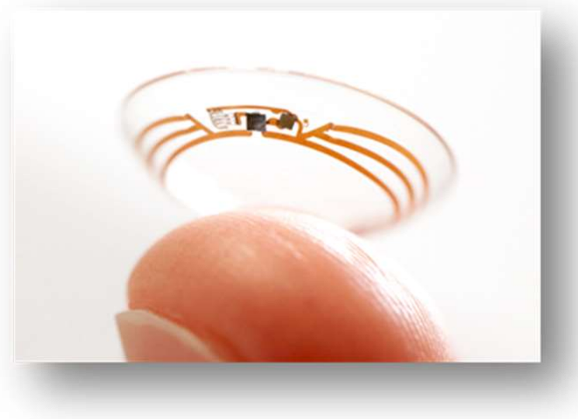
Low voltage power supplies

Systems beyond Li/LiPON/$LiCoO_2$

- New material optimized solutions for generic needs:

  - Improved capacity per surface/volume unit
  - Lower operating voltages
  - Use of thermally sensitive substrates





Systems beyond $Li/LiPON/LiCoO_2$

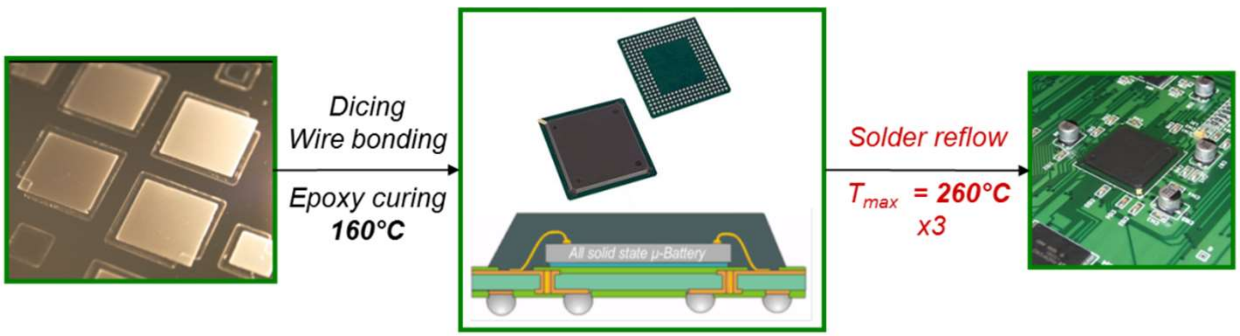
- New material optimized solutions for generic needs:

Improved capacity per surface/volume unit

Lower operating voltages

Use of thermally sensitive substrates

Solder reflow tolerance



µ-batteries on Si wafer — Integration in a BGA/LGA package — Connection on the PCB

Systems beyond Li/LiPON/$LiCoO_2$

- New material optimized solutions for generic needs:

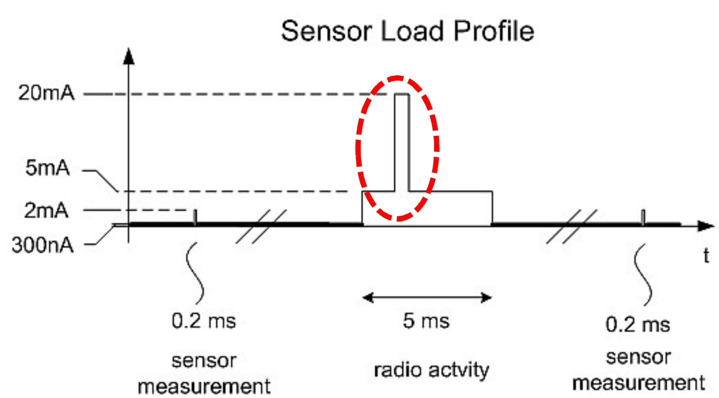
Improved capacity per surface/volume unit

Lower operating voltages

Use of thermally sensitive substrates

Solder reflow tolerance

Lower impedance



Systems beyond $Li/LiPON/LiCoO_2$

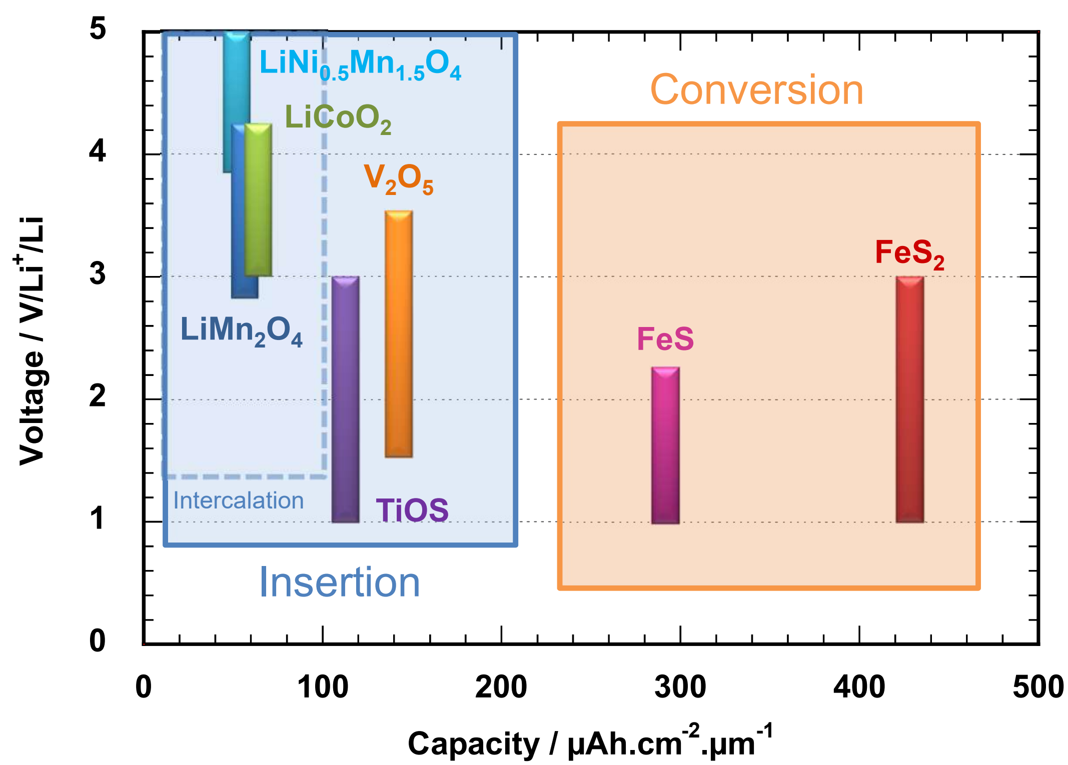
- New material optimized solutions for generic needs:

Improved capacity per surface unit

- Surface capacity limited by the cathode material ➡ replacement of $LiCoO_2$
- Higher volumetric capacity ➡ cost reduction / µAh

➡ Insertion compound able to insert/deinsert more Li ions, with anions participating to the redox process (TiOS)

➡ Material reacting with Li according to a conversion process (FeS_2)

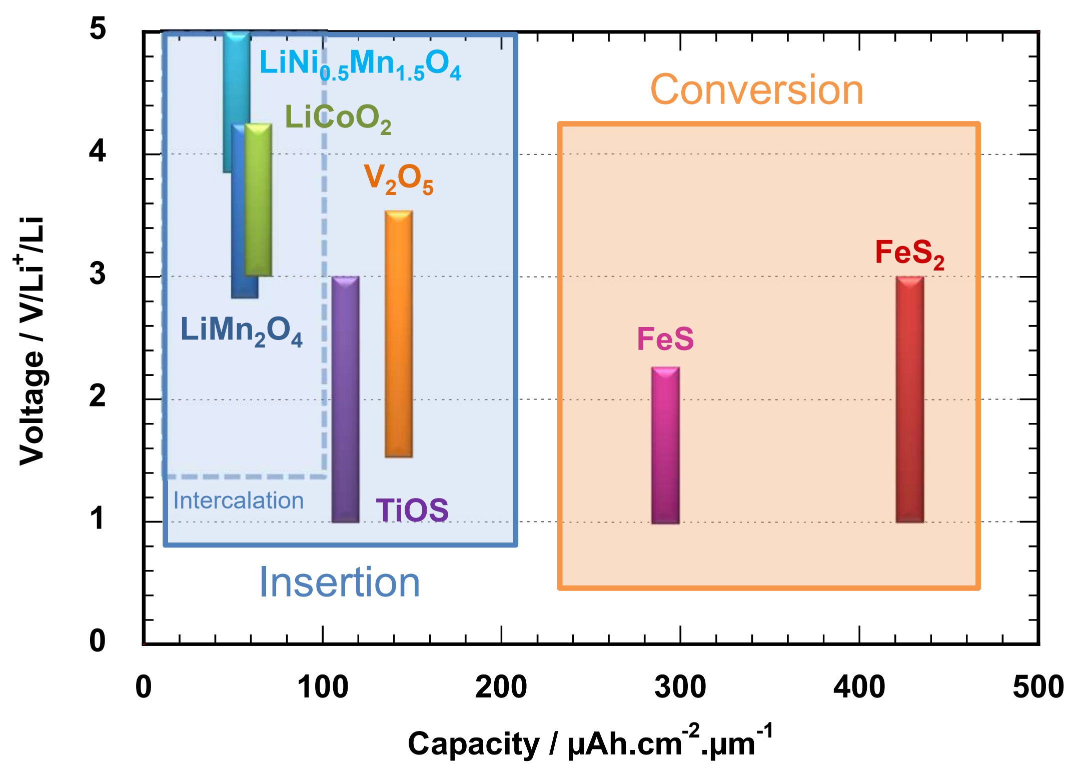


Systems beyond $Li/LiPON/LiCoO_2$

- New material optimized solutions for generic needs:

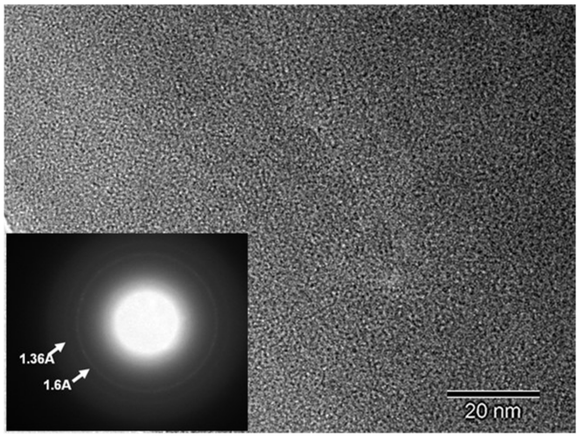
Improved capacity per surface unit
Lower operating voltage
Use of thermally sensitive substrates

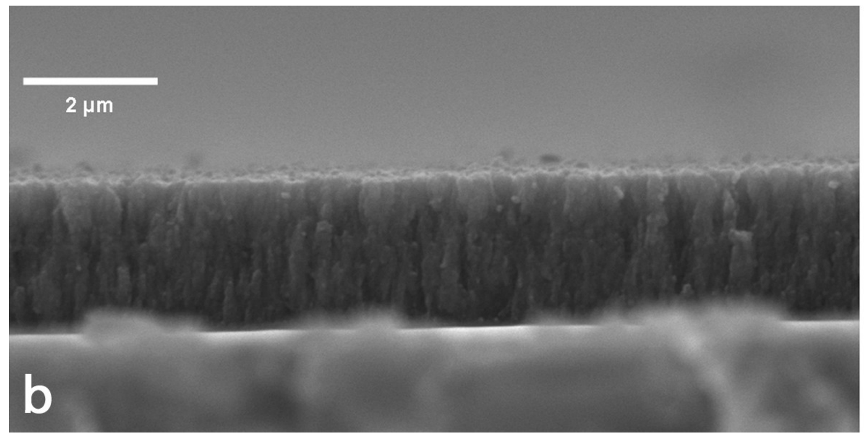
- ⇨ Insertion compound able to insert/deinsert more Li ions, with anions participating to the redox process (TiOS)
- ⇨ Material reacting with Li according to a conversion process (FeS_2)



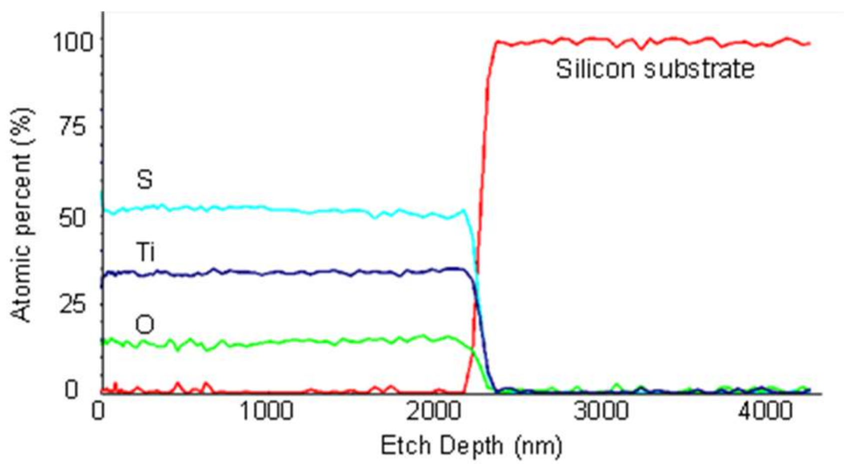
Titanium oxysulfide positive electrodes

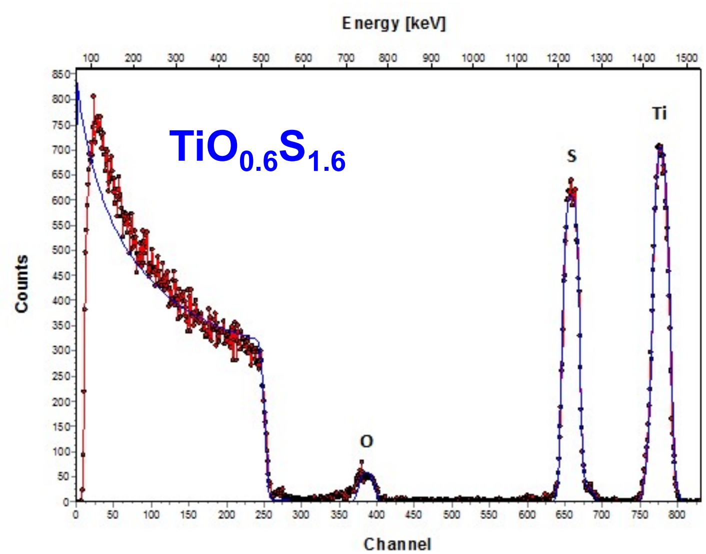
- TiS_2 target sputtered under Ar
- Amorphous film with columnar growth. No annealing required.





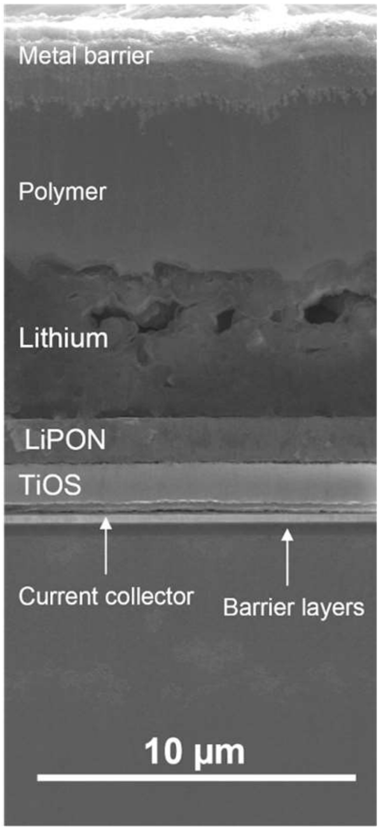
- Homogeneous composition over the whole thickness. Composition close to $TiO_{0.6}S_{1.6}$

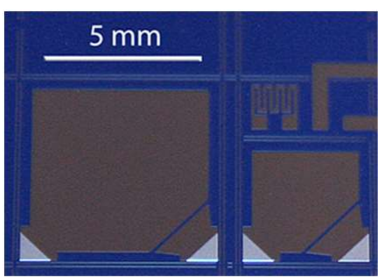




Li/LiPON/TiOS microbatteries

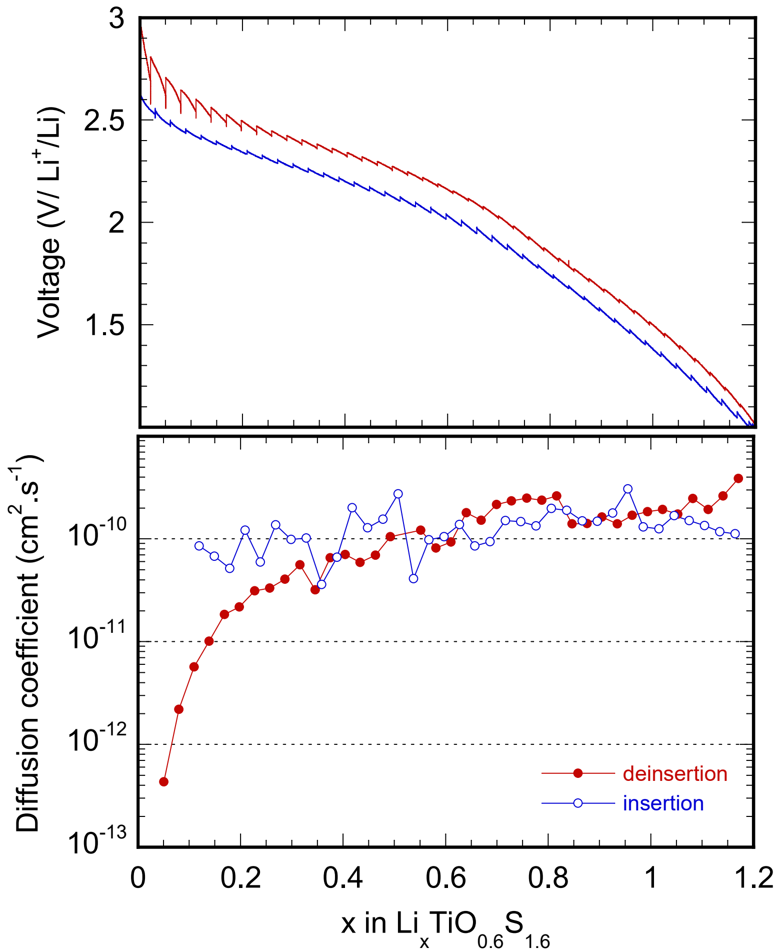
- GITT measurements on an all-solid-state stack:





- 1.2 Li per $TiO_{0.6}S_{1.6}$ reversibly exchanged

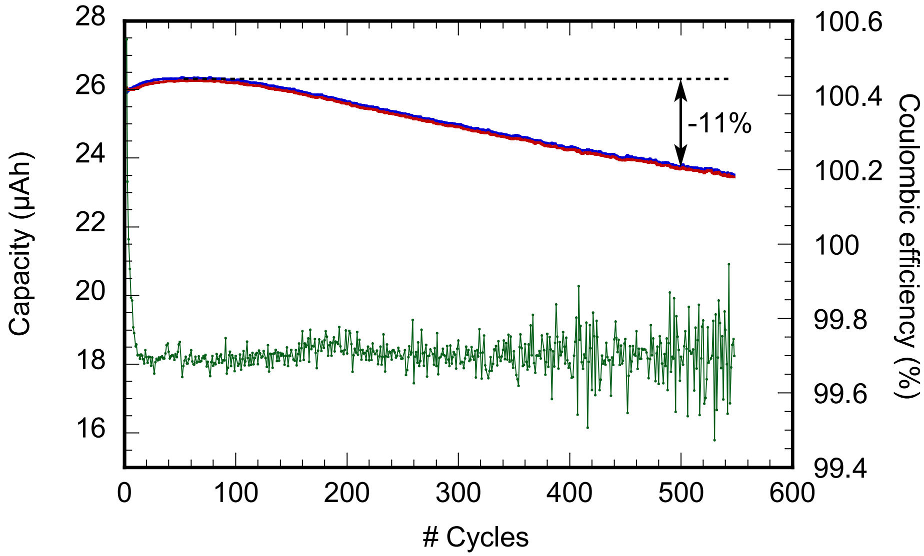
- High Li diffusion coefficient $5 \cdot 10^{-11}$ - $3 \cdot 10^{-10}$ $S \cdot cm^{-1}$ at 20°C ≫ $LiCoO_2$ (10^{-13} - 10^{-11} $S \cdot cm^{-1}$)

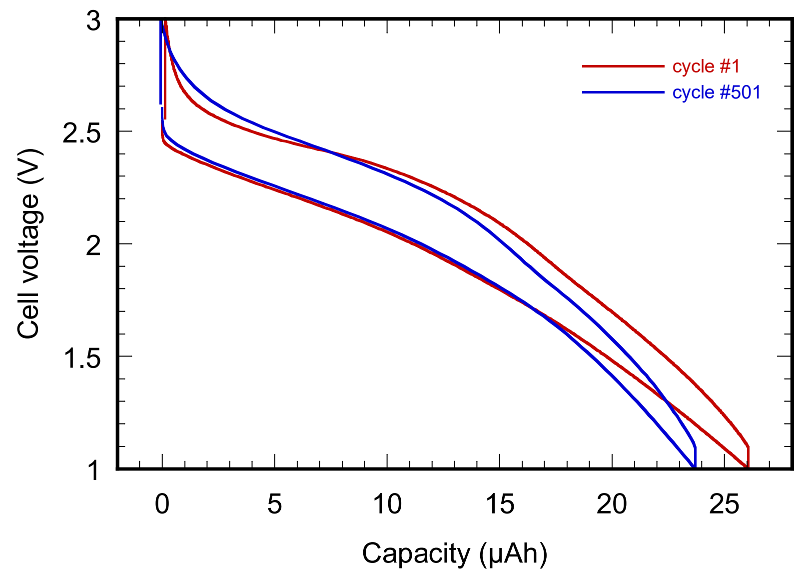


B. Fleutot, B. Pecquenard, F. Le Cras, B. Delis, H. Martinez, L. Dupont, D. Guy-Bouyssou, *J. Power Sources*, 196, 10289-10296 (2011)

Li/LiPON/TiOS microbatteries

- Galvanostatic cycling (100 μA·cm^{-2} or ~ 1C rate)



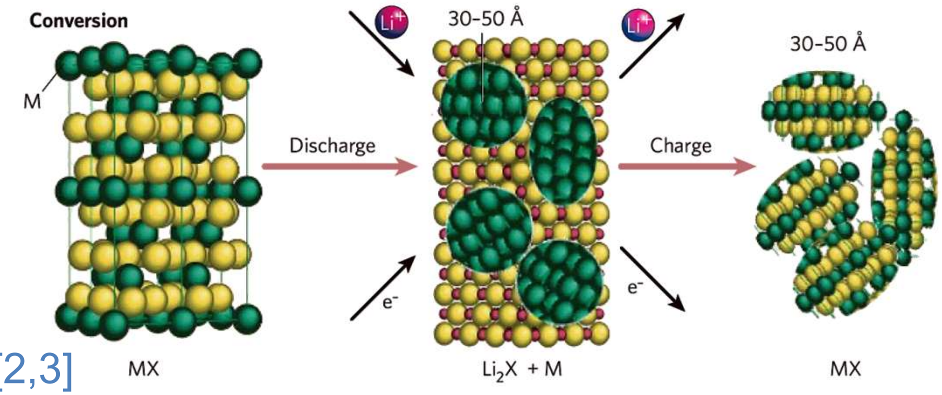


- High volumetric capacity: ~ 90 μAh·cm^{-2}·μm^{-1} >> 64 μAh·cm^{-2}·μm^{-1} for $LiCoO_2$
- Moderate fading (-0.02%/cycle)
- Stable coulombic efficiency ~99.7%
- Less than 2%/year of self-discharge

B. Fleutot, B. Pecquenard, F. Le Cras, B. Delis, H. Martinez, L. Dupont, D. Guy-Bouyssou, *J. Power Sources*, 196, 10289-10296 (2011)

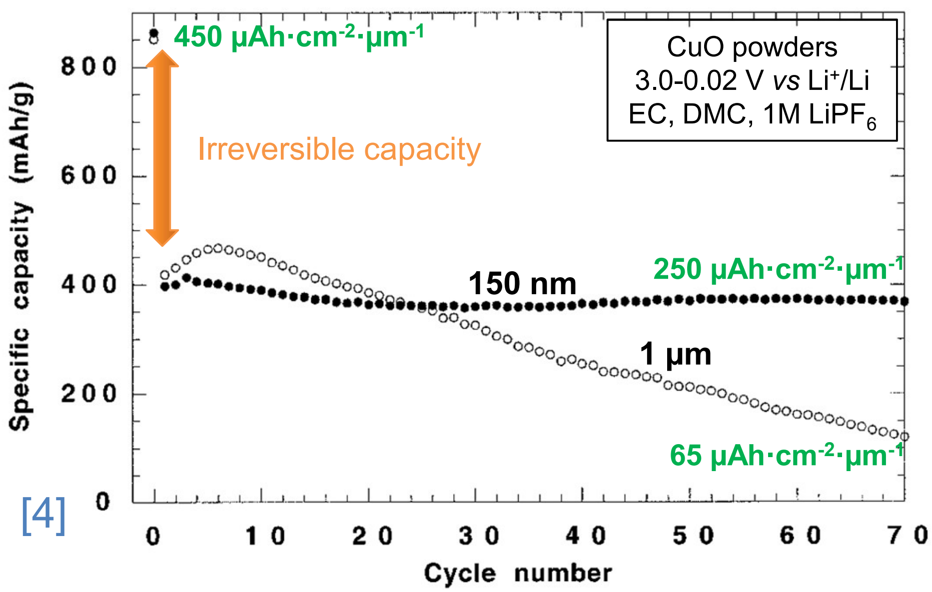
Another way to improve capacity: conversion reactions

- General mechanism [1]: $M_aX_b + (b\cdot n)Li \rightleftharpoons aM + bLi_nX$ M: transition metal
  X: N, O, F, P, S,…



[2,3]

Ex: $CuO + 2Li \rightleftharpoons Cu^0 + Li_2O$



[4]

- Main features:
  - Insertion of 2 to 6 Li^+ per formula unit ➡ high specific capacity
  - Numerous materials can react with Li according to a conversion mechanism ➡ wide range of working potential
  - Large hysteresis between Li insertion /deinsertion process (depending on the M-X bond)
  - Poor reversibility ➡ may be improved by using nanometer size materials

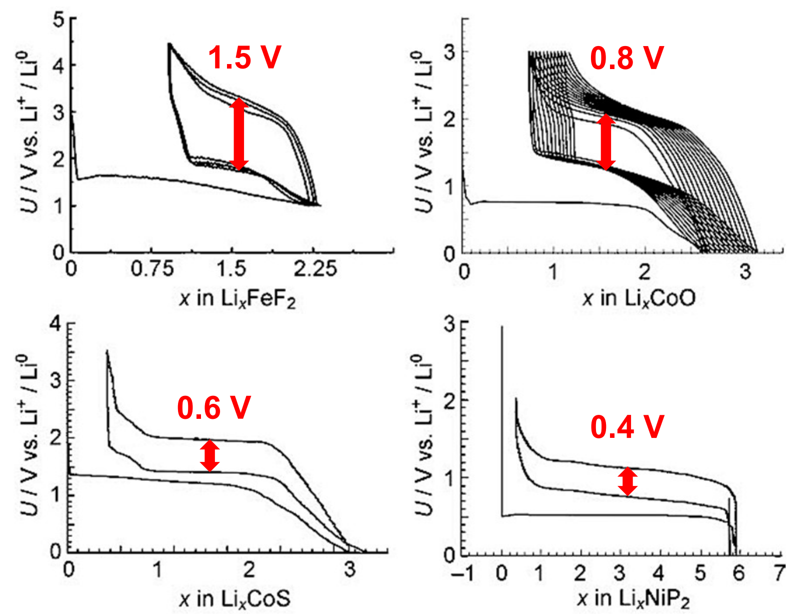
[1] J. Cabana, R. Palacin, L. Monconduit et al., *Adv. Mater.*, 22, E170-E192 (2010); [2] M. Armand and J.-M. Tarascon, *Nature*, 451, 652 (2008)
[3] J. M. Tarascon et al., *C.R. Chimie*, 8, 9 (2005); [4] S. Grugeon et al., *J. Electrochem. Soc.*, 148, A285 (2001)

Iron disulfide positive electrodes

- Why to choose FeS_2 ?

Reaction	$E_{conversion}$ (V)	Capacity ($mAh.g^{-1}$)	Capacity ($\mu Ah.cm^{-2}.\mu m^{-1}$)
$2\ Li + CuO \rightarrow Li_2O + Cu$	1.4	670	426
$2\ Li + Cu_2O \rightarrow Li_2O + 2\ Cu$	1.5	375	225
$2\ Li + CuS \rightarrow Li_2S + Cu$	1.7	560	257
$4\ Li + FeS_2 \rightarrow 2\ Li_2S + Fe$	1.5	894	435

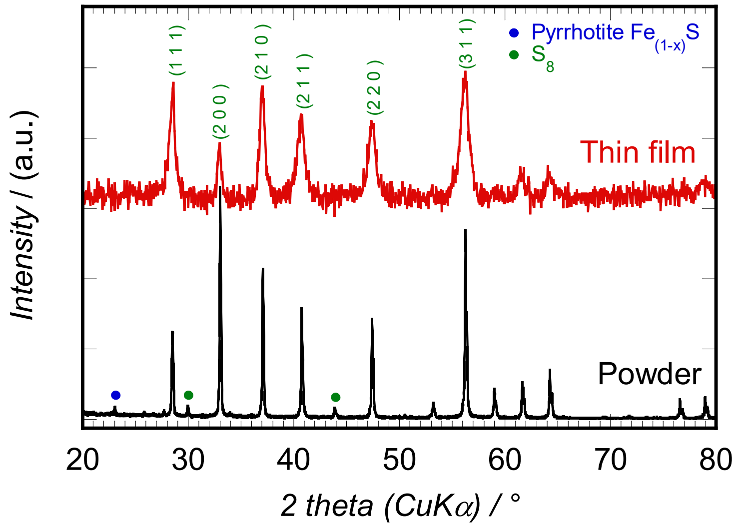
- Theoretical volumetric capacity > 400 $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$ ($LiCoO_2$ x 6)
- Working potential suitable for envisaged applications
- Moderate hysteresis compared to oxides or fluorides
- Ability to be prepared in a thin film form
- No polysulfide dissolution (solid electrolyte)
- Large volume change (+180%) upon lithiation

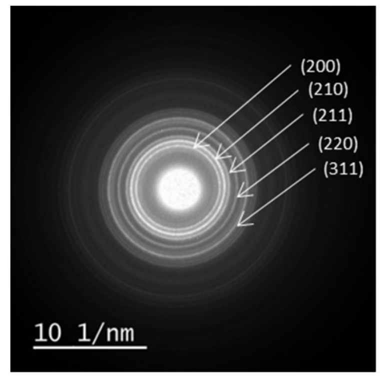


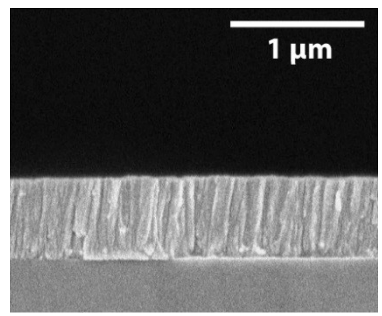
P.G. Bruce, B. Scrosati, J.M. Tarascon, *Angew. Chem. Int. Ed.*, 47 , 2930 (2008)

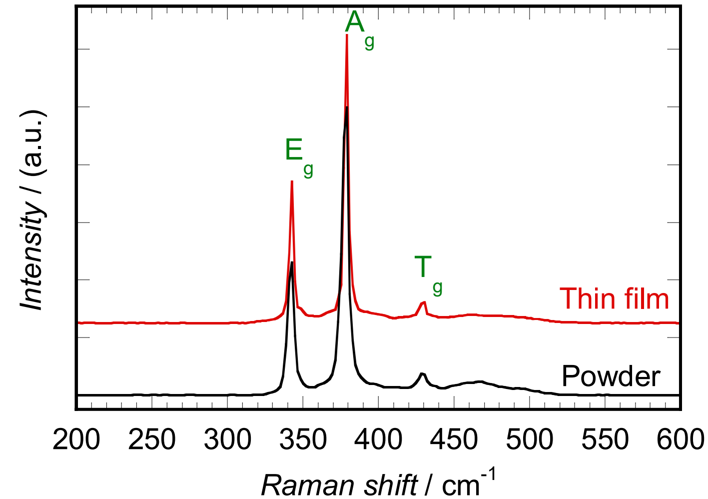
Iron disulfide positive electrodes

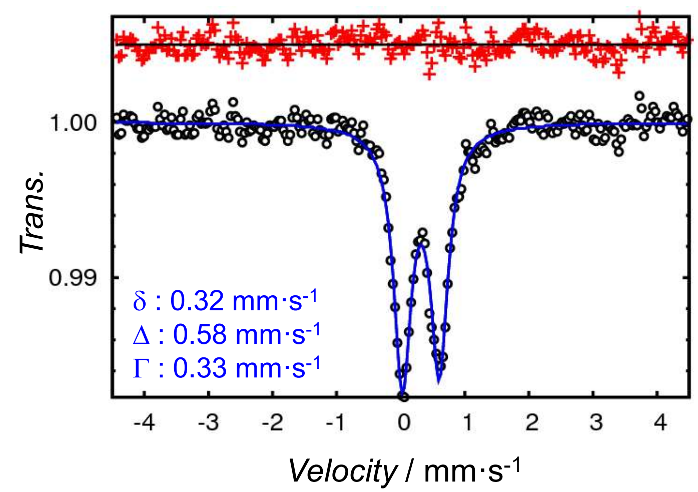
- FeS_2 target sputtered under Ar:











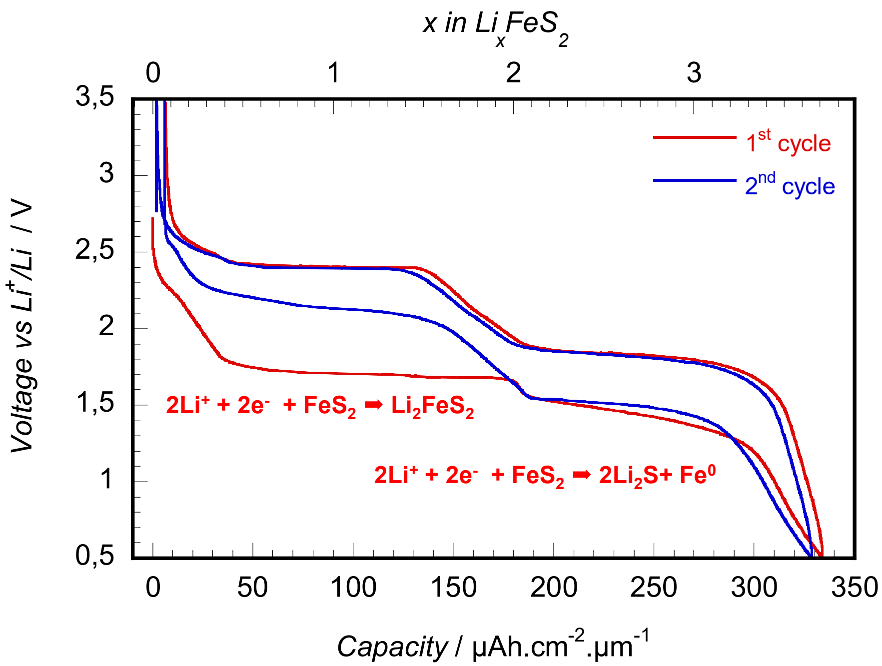
- Well-crystallized thin films
- No pyrrhotite impurity detected in the film
- Fe^{2+} only (Mössbauer) ➡ S_2^{2-} species
- FeS_2 thin films are quite dense (91 % of the theoretical density) and exhibit a columnar
- Good electronic conductivity (51 $S.cm^{-1}$)

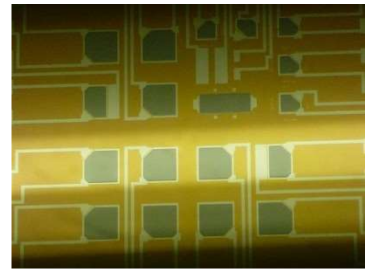
V. Pelé, F. Flamary, L. Bourgeois, B. Pecquenard, F. Le Cras, Electrochem. Comm., 51, 81-84 (2015)

Mössbauer analysis by M. Sougrati, ICG (Montpellier, France)

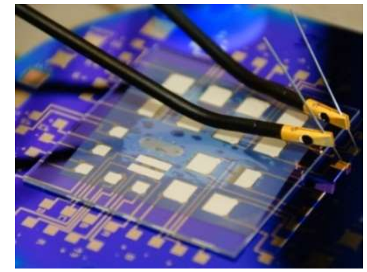
Li/LiPON/FeS_2 microbatteries

- Electrochemical behavior of Li/LiPON/FeS_2 all-solid-state cells :

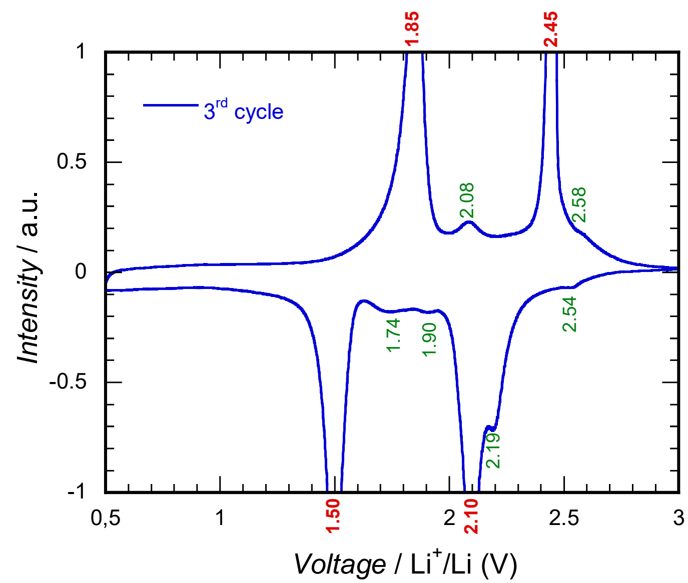




FeS_2 electrodes (365 nm)



Microbatteries

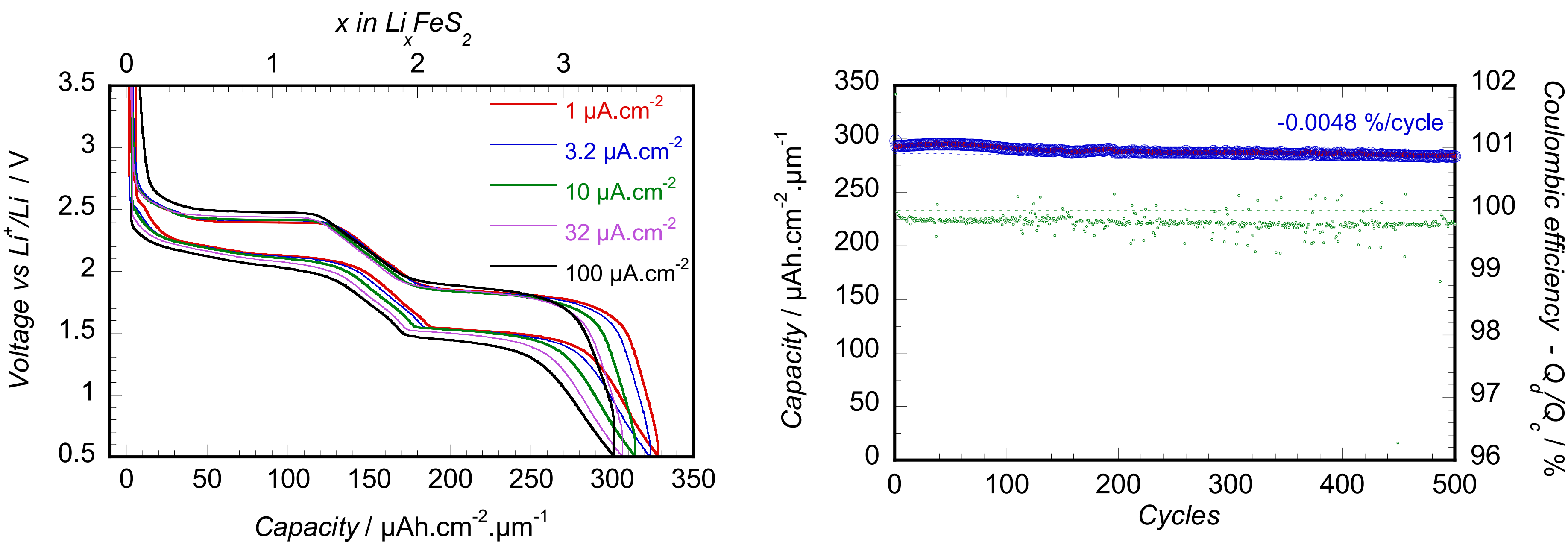


- First discharge:
  - High capacity 330 µAh·cm^{-2}·µm^{-1}
  - Two steps at 1.7 and 1.5 V
- Only 1.8 % of irreversible capacity during the 1st cycle
- Subsequent discharges:
  - Two well-defined steps at 2.15 and 1.5 V
  - Presence of less prominent intermediate reactions ➡ complex processes

V. Pelé, F. Flamary, L. Bourgeois, B. Pecquenard, F. Le Cras, *Electrochem. Comm.*, 51, 81-84 (2015)

Li/LiPON/FeS_2 microbatteries

- Electrochemical behavior of Li/LiPON/FeS_2 all-solid-state cells :



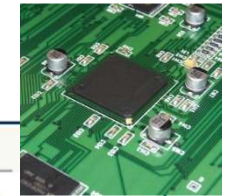
- Limited voltage hysteresis even at high regimes (100 µAh.cm^{-2} ⇆ 1C rate)
- Excellent cycle life with a fading of only -0.0048 %/cycle
- No marked detrimental effect of the large volume expansion (+180%) during Li insertion

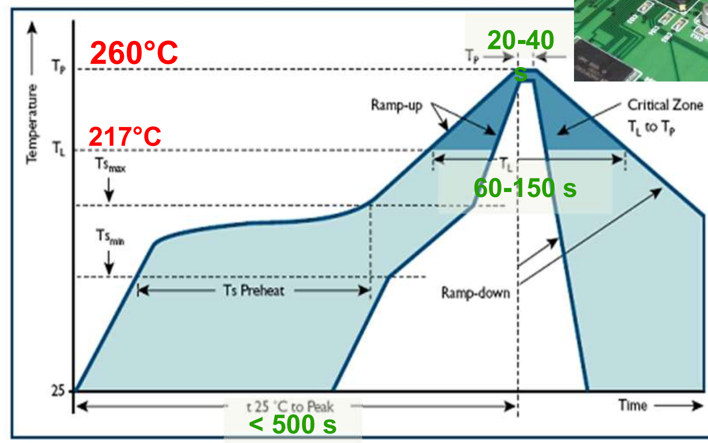
V. Pelé, F. Flamary, L. Bourgeois, B. Pecquenard, F. Le Cras, Electrochem. Comm., 51, 81-84 (2015)

Solder reflow tolerant microbatteries

- New material optimized solutions for generic needs:

Solder reflow tolerance





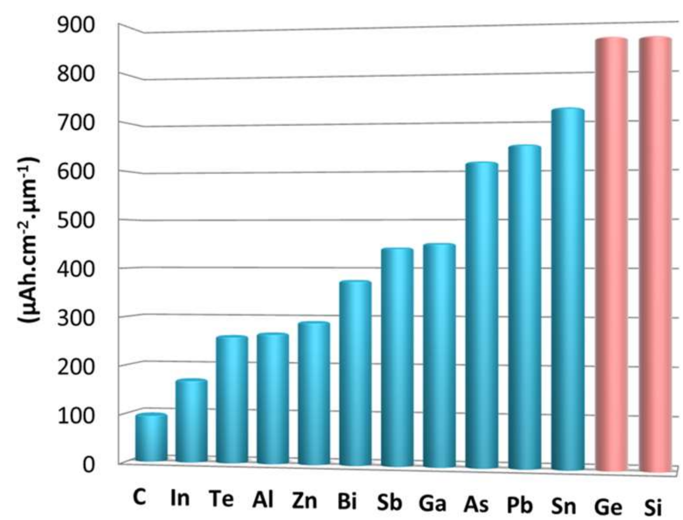
Lead-free (Ag-Sn) solder reflow temperature profile

- Metallic Li melts at 180°C
  - ‘Li-free’ microbatteries
  - Li-ion microbatteries

- Si as negative electrode is very attractive due to
  - a high volume capacity (830 µAh.cm^{-2}.µm^{-1})

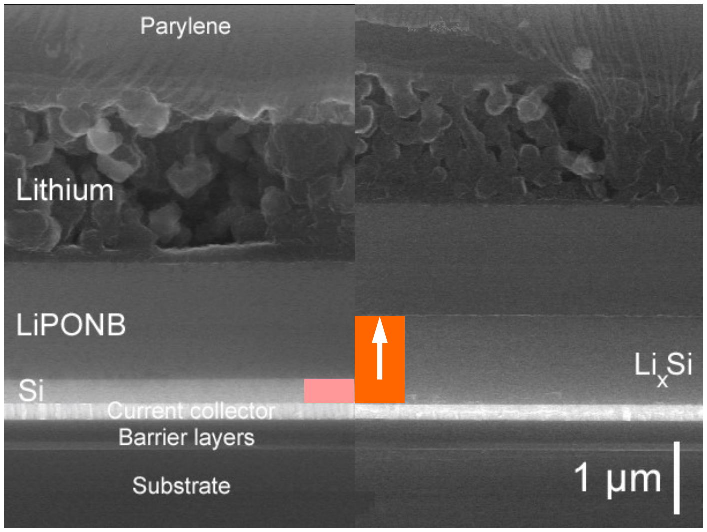
    $$4\ Si + 15\ Li^{+} + 15\ e^{-} \Leftrightarrow Li_{15}Si_{4}$$

  - a low insertion/deinsertion voltage [0.0-1.0] V/Li^{+}/Li
  - an easy deposition by sputtering under Ar



- But …
  - +180% volume expansion ➡ mechanical degradation ?

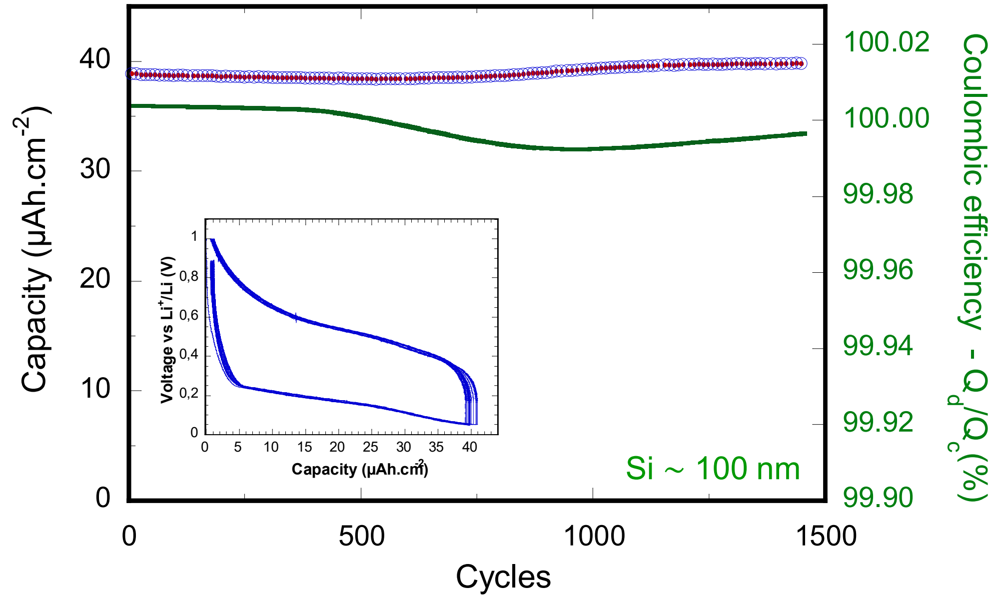
Silicon anode for Li-ion microbatteries



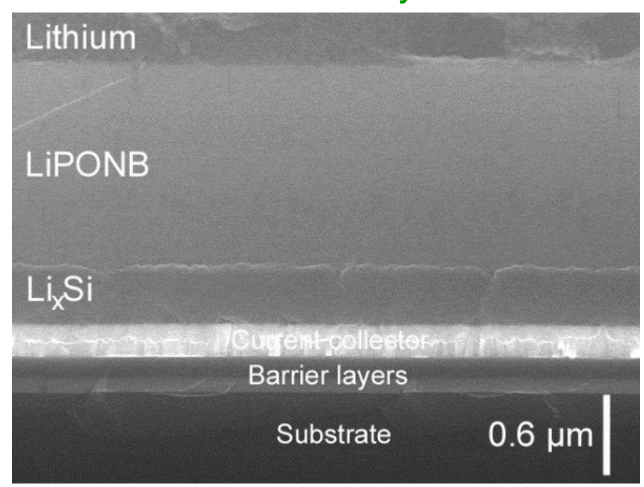
Pristine cell

Si ~ 300 nm

Discharged cell
0 V/Li⁺/Li
Li_xSi ~ 1200 nm



After 1500 cycles

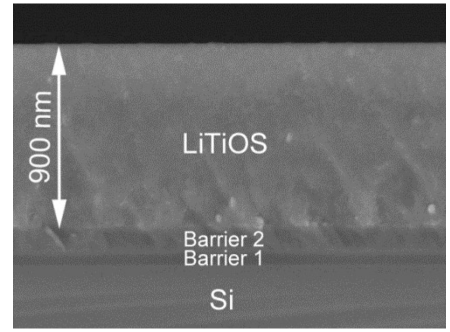


- High cycle life: 1500 cycles with no capacity loss
- Coulombic efficiency > 99.99 %
- Volume expansion (+280%) ⊥ to the substrate
- No mechanical damage even after 1500 cycles for 100 nm thick Si electrodes

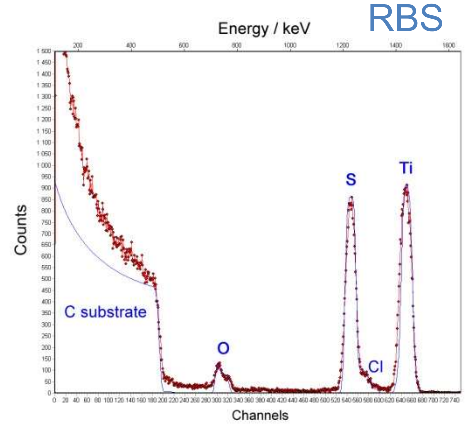
V.P. Phan, B. Pecquenard, F. Le Cras, *Adv. Function. Mater.*, 22, 2580 (2012)

LiTiOS cathodes for Li-ion microbatteries

- Sputtering of a homemade $LiTiS_2$ target ➡ LiTiOS thin films
- Dense & homogeneous thin films

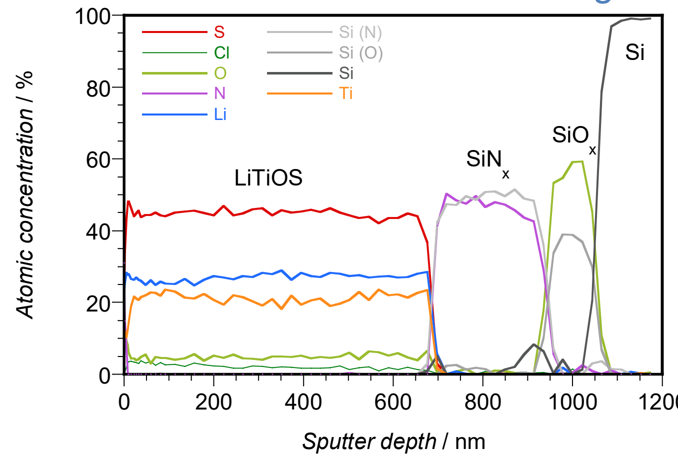


RBS



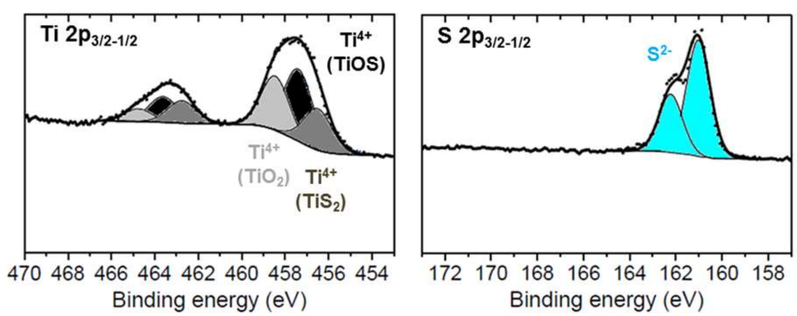
- Composition : $Li_{1.2}TiO_{0.5}S_{2.1}$

Auger



- Contains only Ti^{4+} and S^{2-} species

XPS



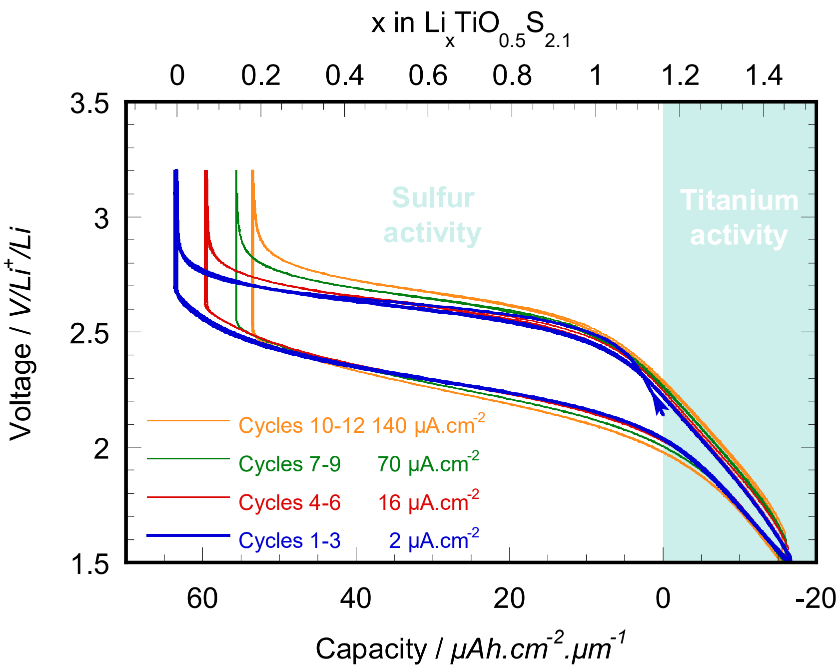
* Collaboration H. Martinez, IPREM Pau, France

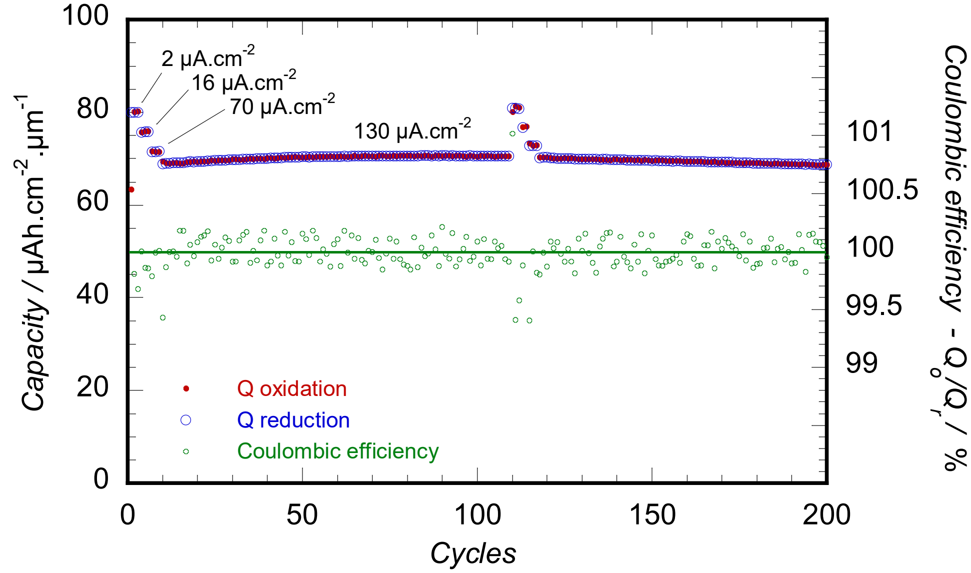
- Oxygen uptake during the deposition

F. Le Cras, B. Pecquenard, V.P. Phan, V. Dubois, D. Guy-Bouyssou, *Adv. Energy. Mater.*, 5, 1501061 (2015)

LiTiOS cathodes for Li-ion microbatteries

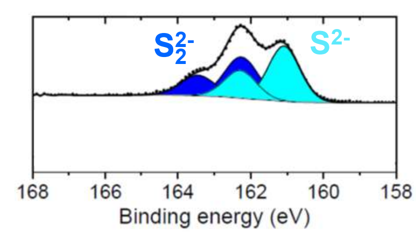
- Electrochemical behavior of Li/LiPON/'LiTiOS' all-solid-state cells :



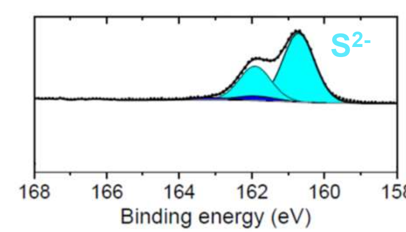


- First charge: $Li_{1.2}Ti^{(4+)}O_{0.5}S_{2.1}^{(2-)} \Leftrightarrow Ti^{(4+)}O_{0.5}S_{0.9}^{(2-)}S_{1.2}^{(-)} + 1.2\ Li^{+} + 1.2\ e^{-}$

- Capacity 65 (80) $\mu Ah \cdot cm^{-2} \cdot \mu m^{-1}$
- Perfect cycle life
- Coulombic efficiency ~ 99.99%
- Increased polarization near the end of charge



End of 1st charge: 3.2V



End of 1st discharge: 2.0V

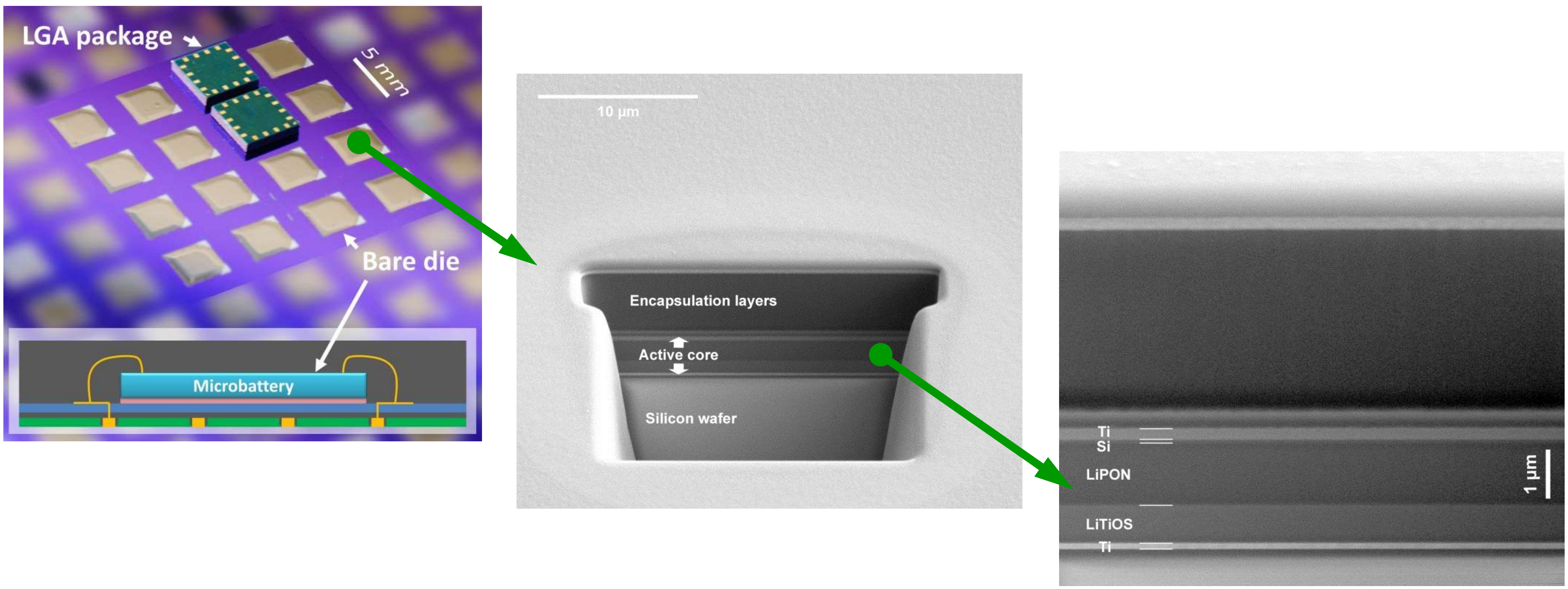
Performance of Si/LiPON/LiTiOS Li-ion microbatteries

- 2 V solid state Li-ion microbatteries:
  - 600-1100 nm $Li_{1.2}TiO_{0.5}S_{2.1}$
  - 1400 nm LiPON
  - 65-120 nm Si

9:1 thickness ratio ⇔ equivalent surface capacity

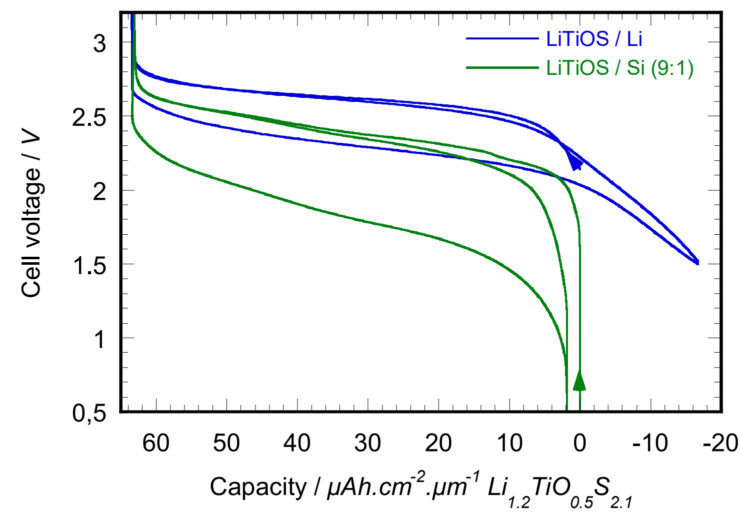
$$Li_{1.2}TiO_{0.5}S_{2.1} + 0.32\ Si \Leftrightarrow TiO_{0.5}S_{2.1} + 0.08\ Li_{15}Si_4$$

- 8.7 mm^2 active area embedded in a 5x5 mm^2 LGA package



Performance of Si/LiPON/LiTiOS Li-ion microbatteries

- Excellent cycle life: -0.005 %/cycle)
- Mean discharge voltage: 1.87 V
- Irreversible capacity: ~ 2%
- No modification of the voltage curve nor the capacity after 3 solder reflow treatments (260°C)

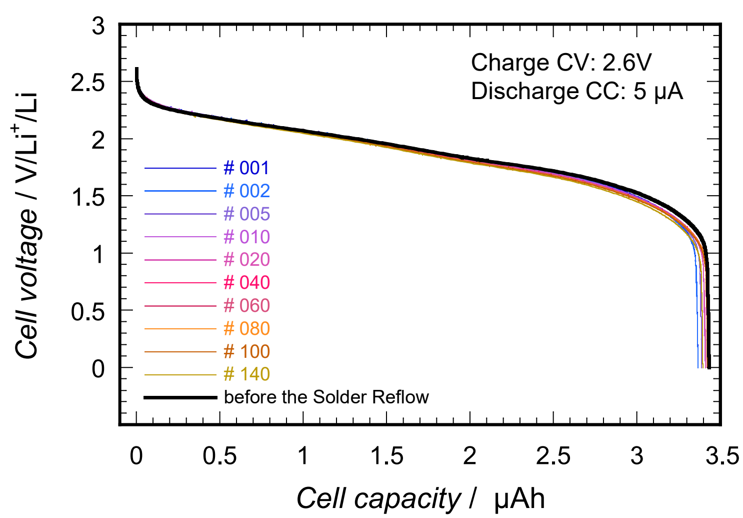


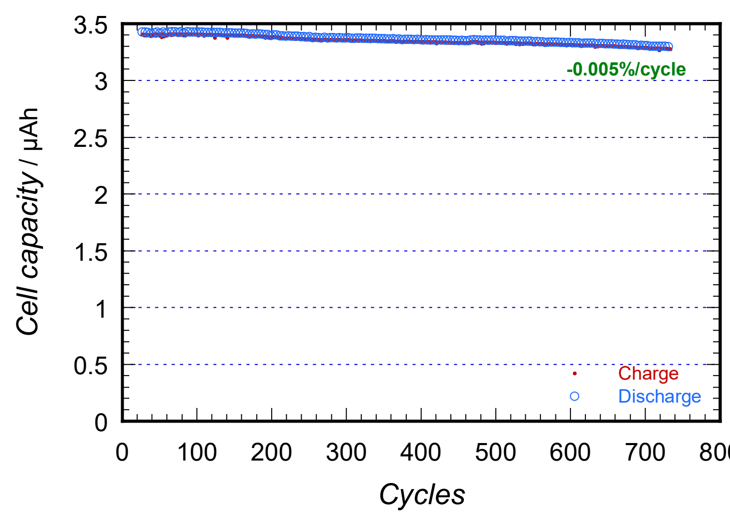
Solder reflow tolerance

Lower operating voltage

Tolerance to short-circuiting

After 3 successive SR treatments





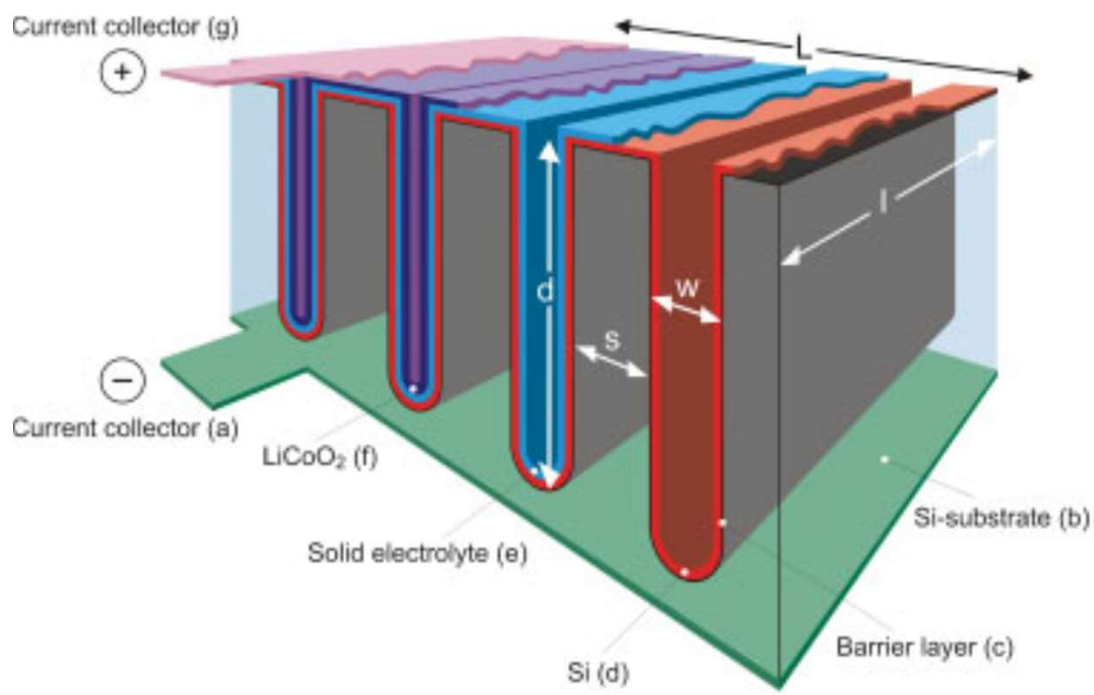
F. Le Cras, B. Pecquenard, V.P. Phan, V. Dubois, D. Guy-Bouyssou, *Adv. Energy. Mater.*, 5, 1501061 (2015)

New designs: 3D solid state microbatteries

- **From planar to high aspect ratio electrodes ⇨ ↗ Areal capacity for a given electrode thickness**

- Capacity ∝ thickness (amount) of electrode material for a given device size
- Limitation in the ionic/electronic transport do not allow to use electrode thicker than 5-10 µm
- Keep usual film thicknesses, but enhance the surface area x *A*

$$A = 1 + 2d\frac{L-s}{L(w+s)}$$



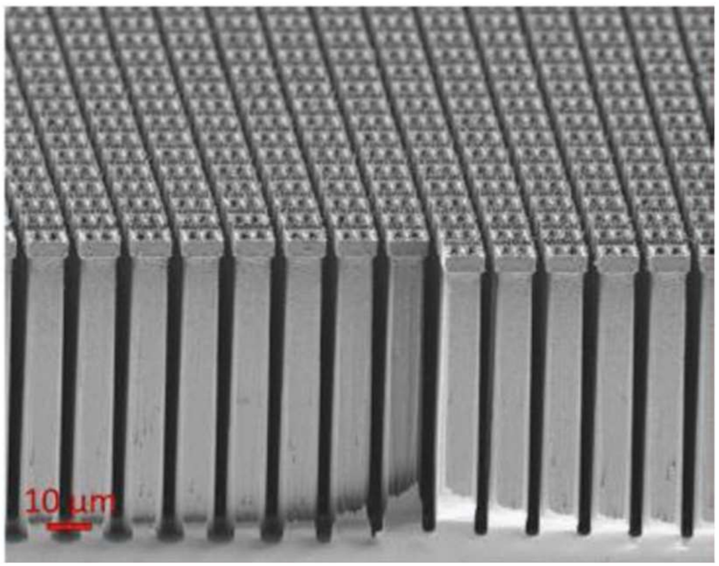
- **Example:**
  - Trench depth = 135 µm
  - Trench width = 5 µm
  - Trench spacing = 5 µm
  - Cathode thickness = 1 µm

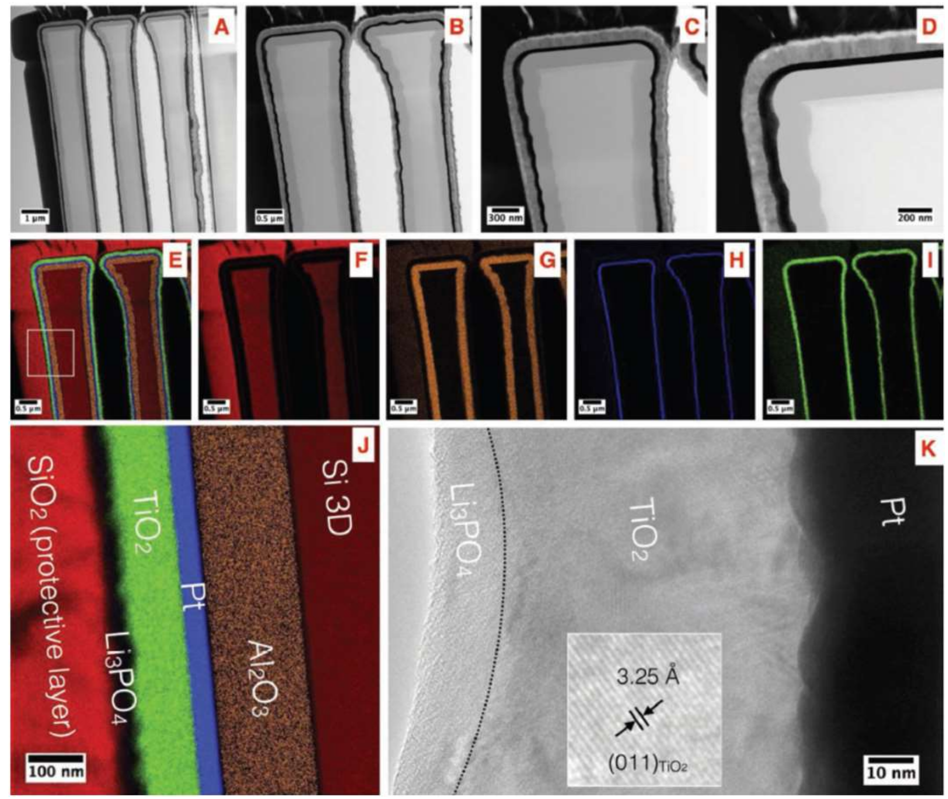
⇨ **Areal capacity x 28**

L. Baggetto et al., *Adv. Funct. Mater.*, **18**, 1-10 (2008)

New designs: 3D solid state microbatteries

- **New preparation and deposition techniques required for high-aspect ratio ‘3D’ microbatteries**
  - Substrates: Deep reactive ion-etching (aspect ratio 20 - 80)
  - Active layers (<100 nm): Atomic layer deposition or Low-pressure CVD
  - Li_3PO_4 not LiPON



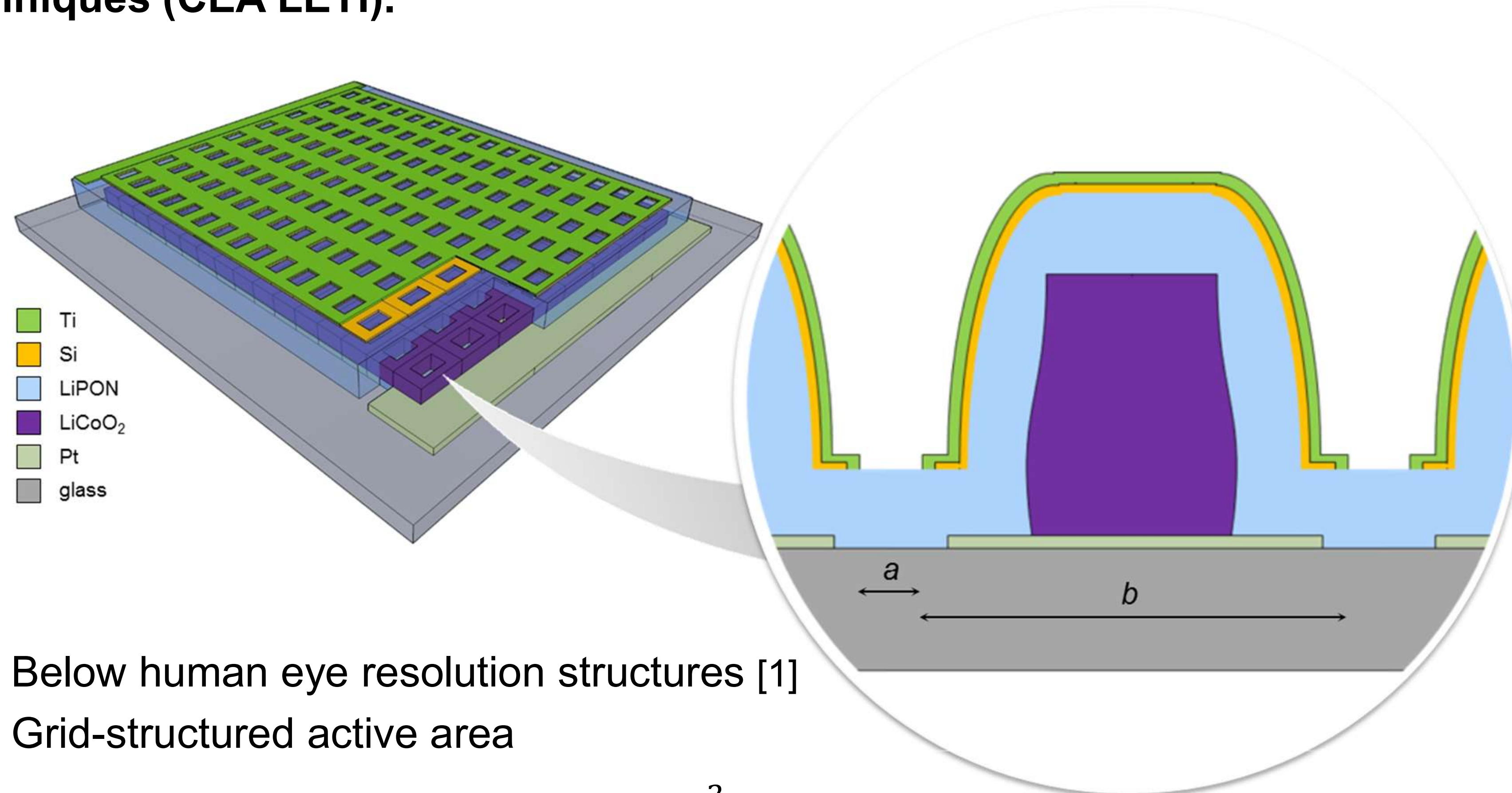


  - No complete 3D solid-state cell achieved yet
  - Electrode capacity (TiO_2 100 nm AR: 50): 370 $\mu Ah.cm^{-2}$

M. Lériche, *Adv. Energy Mater.*, **7**, 1601402 (2017)

New designs: Transparent all-solid-state microbatteries

- **Geometric engineering of battery materials + advanced microfabrication techniques (CEA LETI).**



- Below human eye resolution structures [1]
- Grid-structured active area

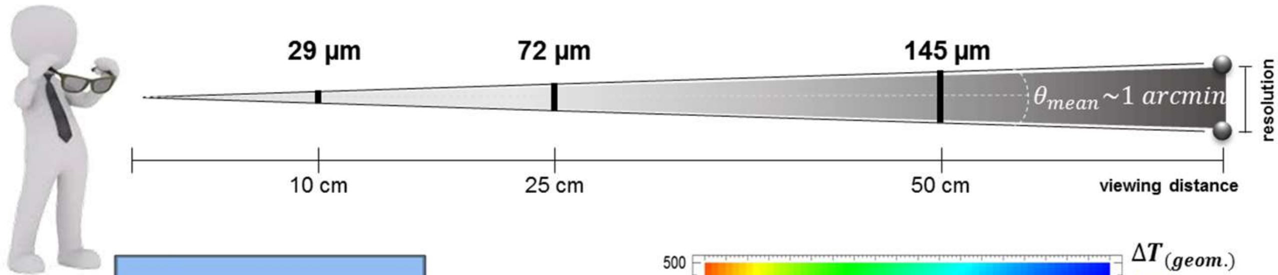
$$\%T_{geometric} = \left(\frac{a}{a+b}\right)^2$$

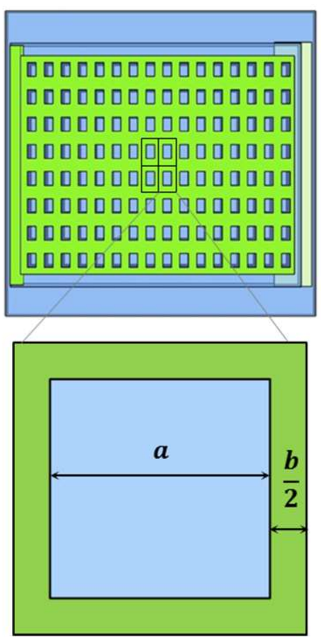
- PVD deposition, patterning using photolithography / etching (dry/wet) techniques for all levels

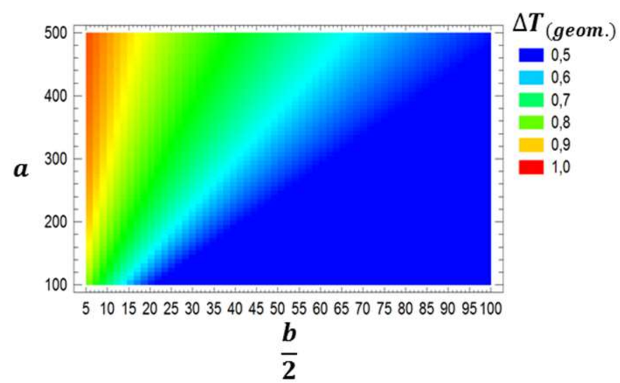
[1] Y. Yang et al., *Proc. Nat. Acad. Sci.*, **108**, 13013–13018 (2011)

New designs: Transparent all-solid-state microbatteries

- **Transparent TFB structures/design:** application driven insofar as resolution is correlated to viewing distance.
- Here: Pattern covering 20-60% total transmittance for >50cm viewing distance applications



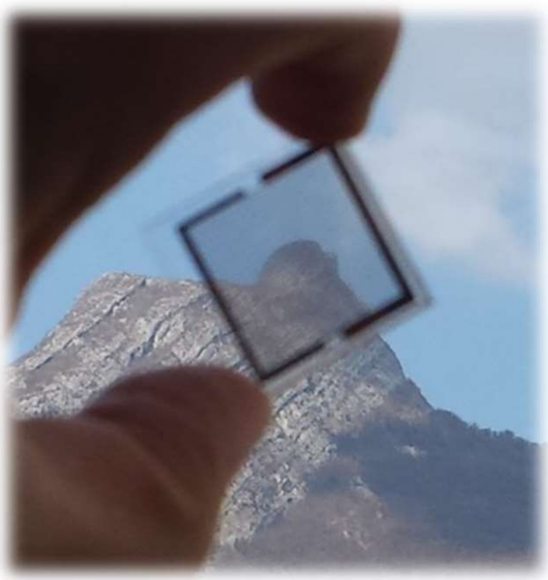


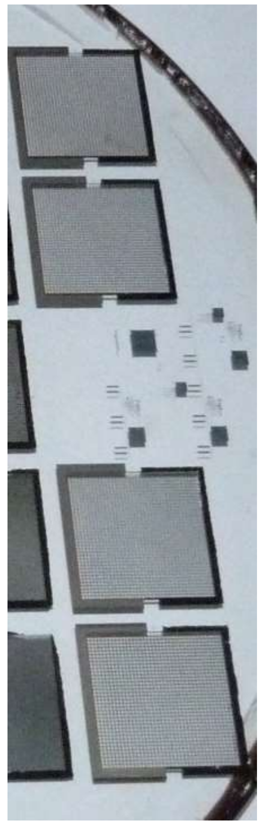


TFB architecture	b/2	a	Theoretical T (%)
A	75	280	18,32
B	65	260	21,25
C	55	240	24,94
D	65	360	31,74
E	85	600	41,65
F	45	220	29,68
G	45	520	60,45

New designs: Transparent all-solid-state microbatteries

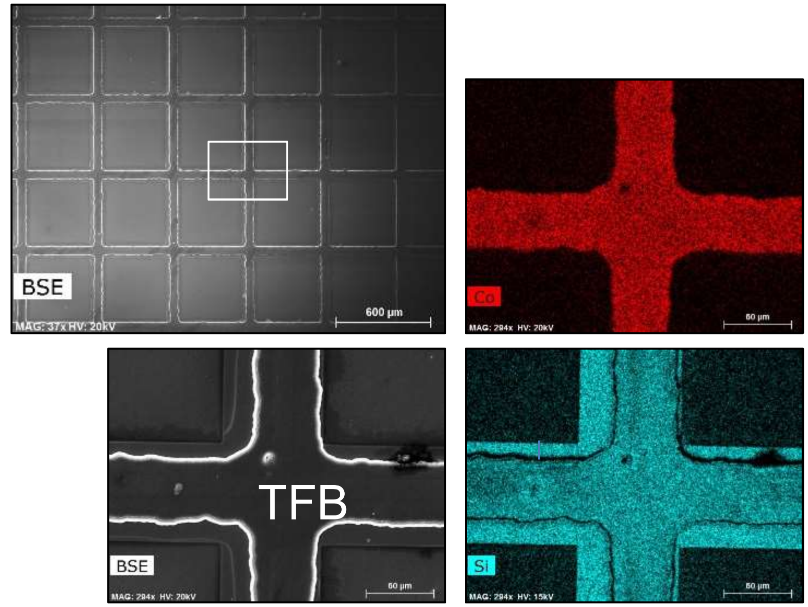
- **Transparent TFB structures/design**



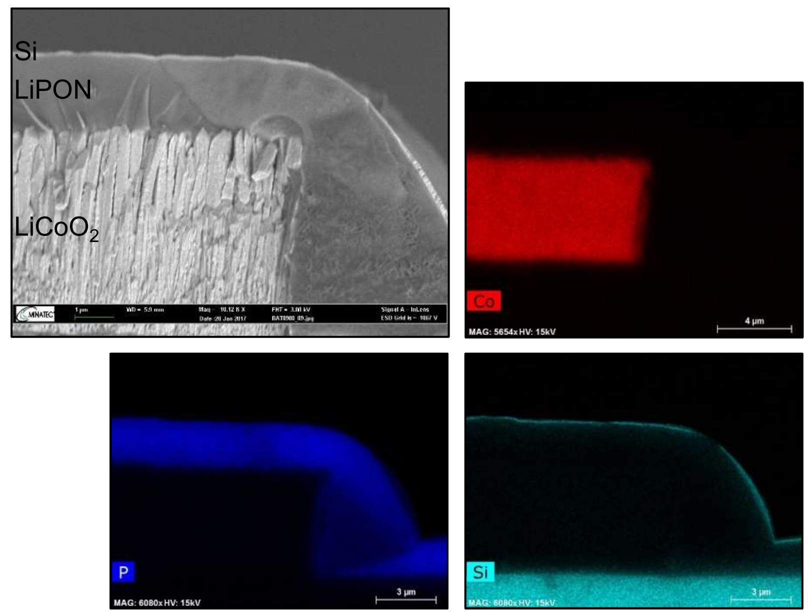


TFBs (1"x1")

Top view (SEM/EDS)



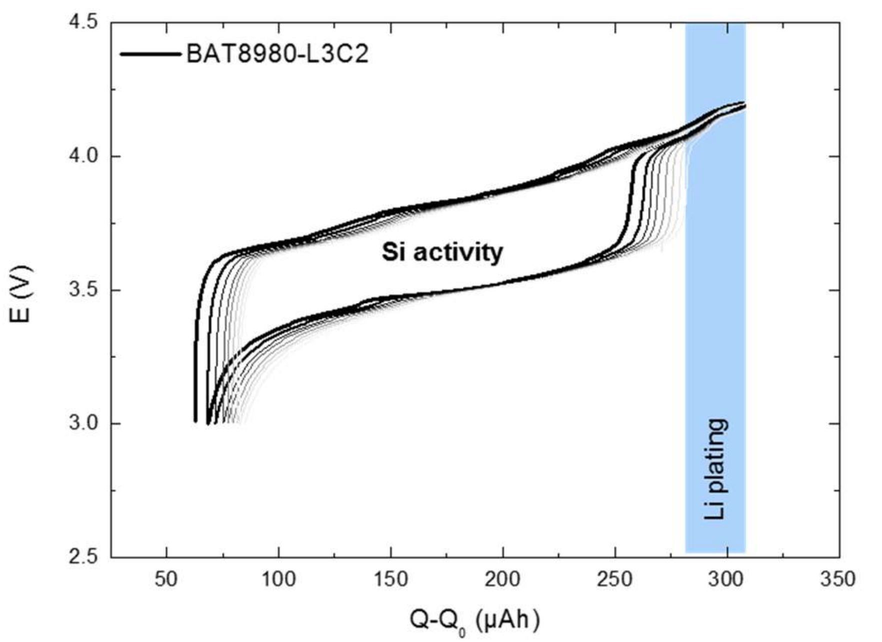
X-section (SEM/EDS)



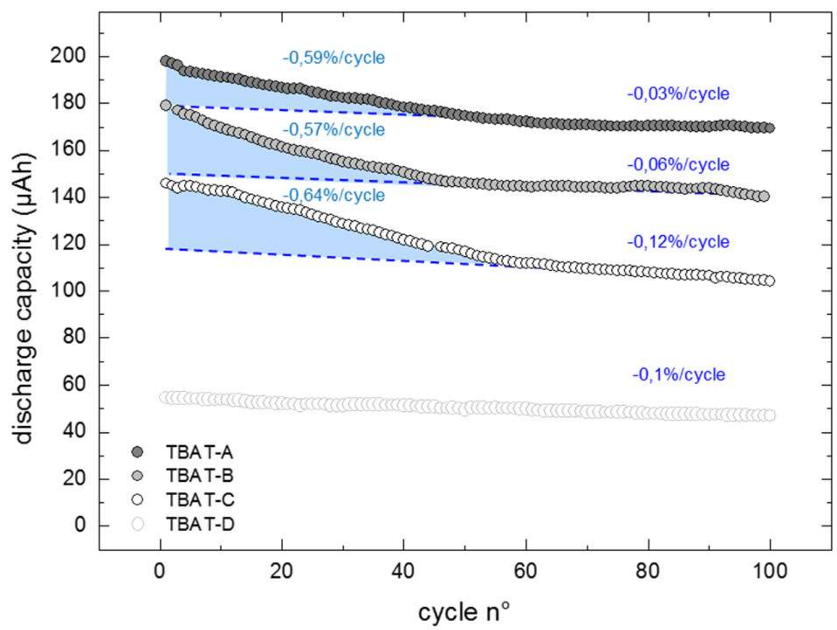
New designs: Transparent all-solid-state microbatteries

- **Features:**
  - Capacity: up to 500 µAh (20 x 20 cm²) ⇔ 60% transmittance
  - Nominal voltage: 3,4 V
  - Low capacity fading after 50 cycles (-0.1%/cycles)
  - Linear relationship between capacity, LCO surface area and transmittance

Galvanostatic cycling within [3-4.2V] at 30µA; cycle 2-10



Discharge capacity variation during first 100 cycles
(CA charge at 4,2V, galvanostatic discharge at C/2)



Summary

- All-solid-state microbatteries are mostly dedicated to applications requiring a **reduced footprint**, a **high level of integration**, and a **limited embarked energy** (10 μWh – 1 mWh)

- **Manufacturing process** similar to those used in the microelectronics industry (sputtering, evaporation, photolithography,…) is **quite expensive** compared to other battery manufacturing process ⇨ high throughput is compulsory:
  - Thin / High volumetric capacity electrodes
  - Reduced number of manufacturing steps
  - The smaller the footprint the higher the throughput…

- **(Li)/LiPON/$LiCoO_2$ system** is the most common active stack in commercial cells

- Particular specifications (voltage, areal capacity, thermal resistance, shape, cost…) can be met by developing appropriate **materials**, **patterning process**, **process flow**.

Summary

- So far, no high capacity 3D all-solid state microbatteries have been achieved. Besides, their cost should be even higher than conventional planar cells.

- Other important topics to consider (not detailed above):
  - Electrode/electrolyte interfaces (reactivity, charge transfer)
  - Alternative materials to LiPON with higher ionic conductivities

Questions ?