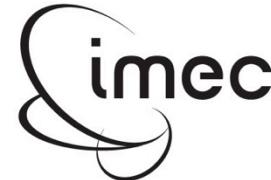


Paving the way towards solid-state 3D thin-film Li-ion batteries

Philippe M. Vereecken, Maarten Mees, Alfonso Sepulveda

Marina Timmermans, Brecht Put, Nouha Labyedh, Sébastien Moitzheim,
Stanislaw Zankowski and Xubin Chen



ASPIRE
INVENT
ACHIEVE

THE BATTERY IS THE LIMITING FACTOR IN TECHNOLOGY

The emergence of Li-ion battery has enabled new applications which emerged and evolved over the last decade...

Portable electronics



High Energy density of Li-ion = portable energy source can be made small enough

Automotive

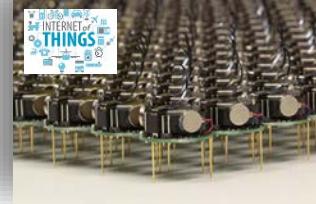


Storage



And will continue to do so for future electronics.

Form factor, Safety, and Fast charging are needed for future developments



IoT



Wearables



Health



Flexible electronics

APPLICATION SPECTRUM IS WIDENING

Rechargeable Li-ion batteries

Power on board



Back-up power chip or PCB

Portable electronics



Hobby and power tools

Vehicles



Bikes, automotive, aviation, rail,...



Wireless sensor networks



distributed wireless sensors and communicators...

Mobile-IT



Smart watch, phones, tablets, PC's

Renewable Energy



Home storage, micro-grid storage, grid storage

Wearable and Flexible



Smart carts, patches, wearables and flexible electronics...

< mWh <

IE-04

IE-03

IE-02

IE-01

< Wh <

IE+00

IE+01

IE+02

< kWh <

IE+03

IE+04

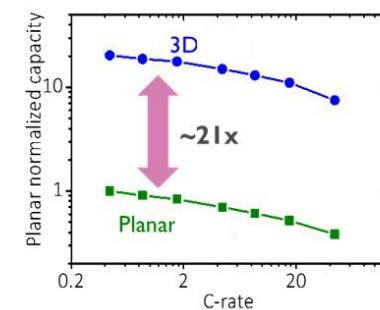
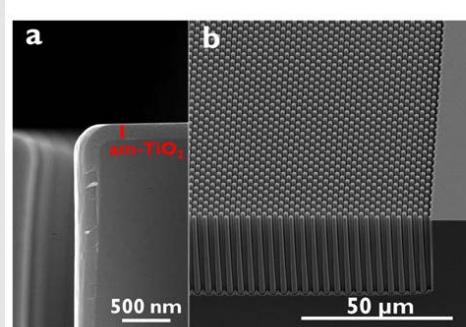
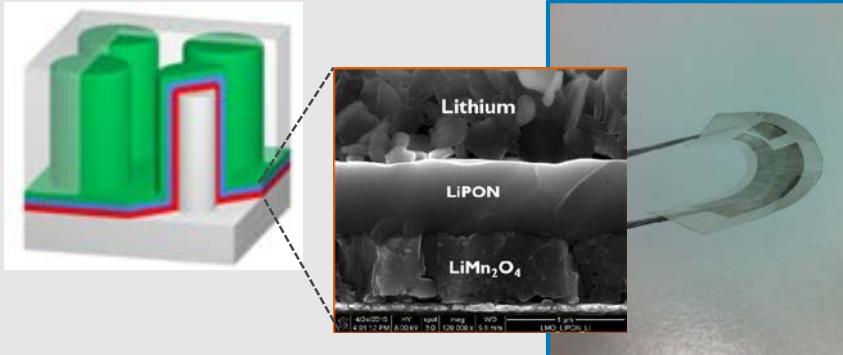
IE+05

< MWh <

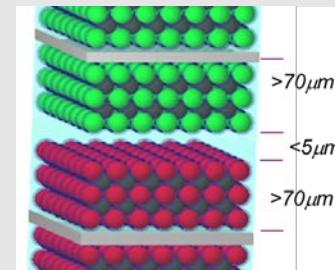
IE+06

IMEC WORKS ON SOLID-STATE BATTERIES

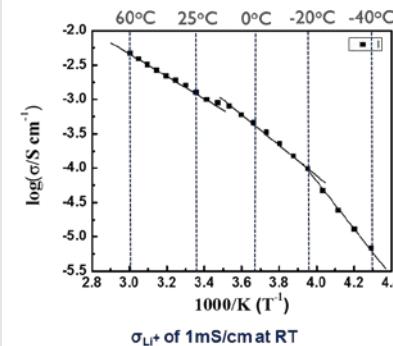
Thin-Film batteries



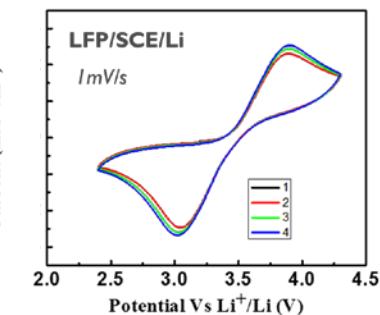
Particle composite batteries



Imec nanocomposite electrolyte



Imec Solid-state Li-ion cell



SOLID STATE ENABLES NEXT GENERATION BATTERIES

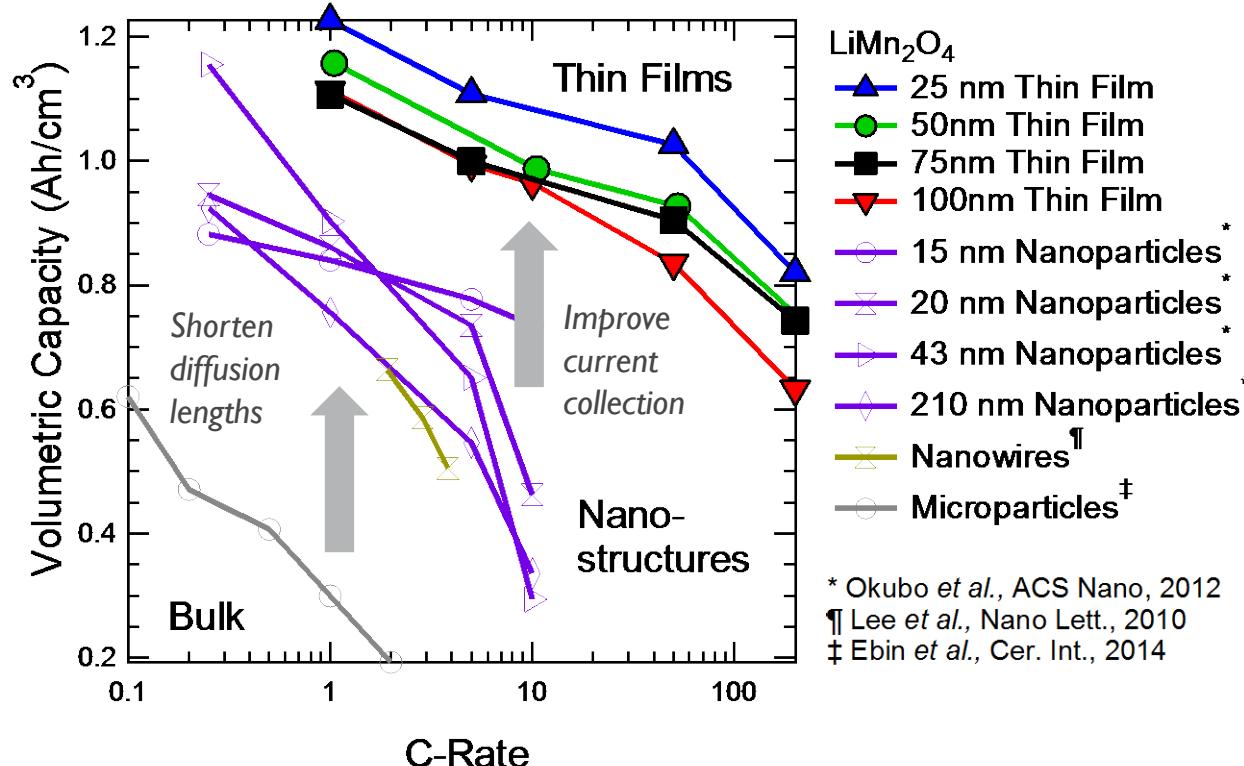
WITH NANOTECHNOLOGY

- Solid-state enables **nanoscaling** of materials (*and thus faster charging kinetics*)
 - The large surface area of nanostructures provide large surface area for fast kinetics for fast charging but also for the parasitic reactions with the liquid electrolyte (dissolution and SEI formation). These side reactions are not an issue for solid-state electrolytes.
- Solid-state enables new ways to increase **energy and power density**
 - Through compacter cells
 - Introduction of high voltage cathodes
- Solid-state enables **miniaturization and integration**
 - Micro-batteries for IoT and wearables
- Solid-state provides **safety**
 - Elimination of the flammable solvent and of the risk of leakage (implants)

IMPROVED RATE PERFORMANCE AT THE NANOSCALE

SOLID ELECTROLYTE PREVENTS DEGRADATION OF THE NANOMATERIAL

- Example of LiMn_2O_4 or LMO as positive electrode with cubic spinel structure

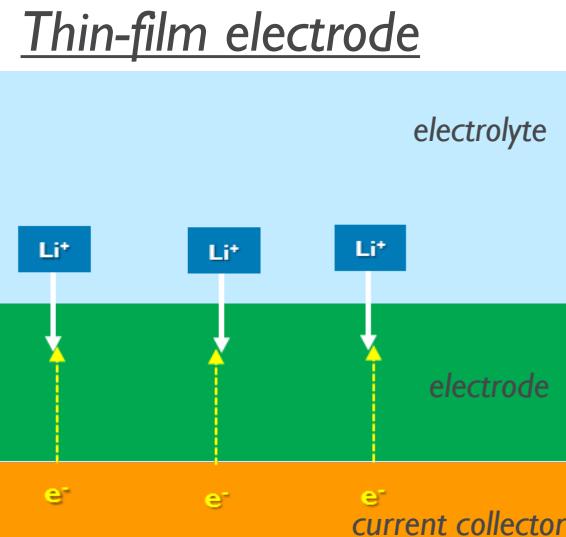
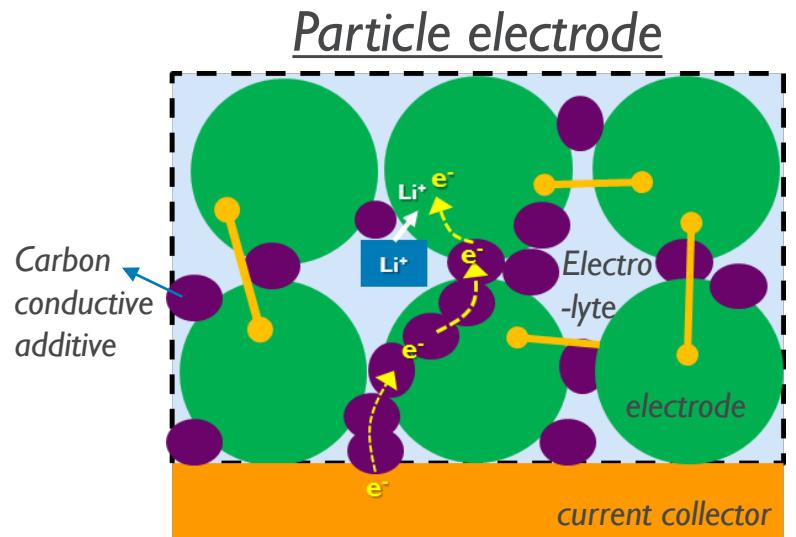


"High cycling stability and extreme rate performance in nanoscaled LiMn_2O_4 thin films" B. Put, P. M. Vereecken N. Labyedh, A. Sepulveda, C. Huyghebaert, I. P. Radu, and A. Stesmans, *ACS Appl. Mater. Interfaces*, 7, 1944-8244 (2015). DOI: 10.1021/acsami.5b06386

BEST CASE CURRENT COLLECTION FOR THIN-FILMS

THIN-FILMS ARE IN DIRECT CONTACT WITH THE CURRENT COLLECTOR

- Shorter diffusion lengths for Li^+ and electrons provides faster charger for nanoscaled active materials (nanoparticles, nanorods and thin films)
- Good current collection is needed to fully enable the fast charging properties



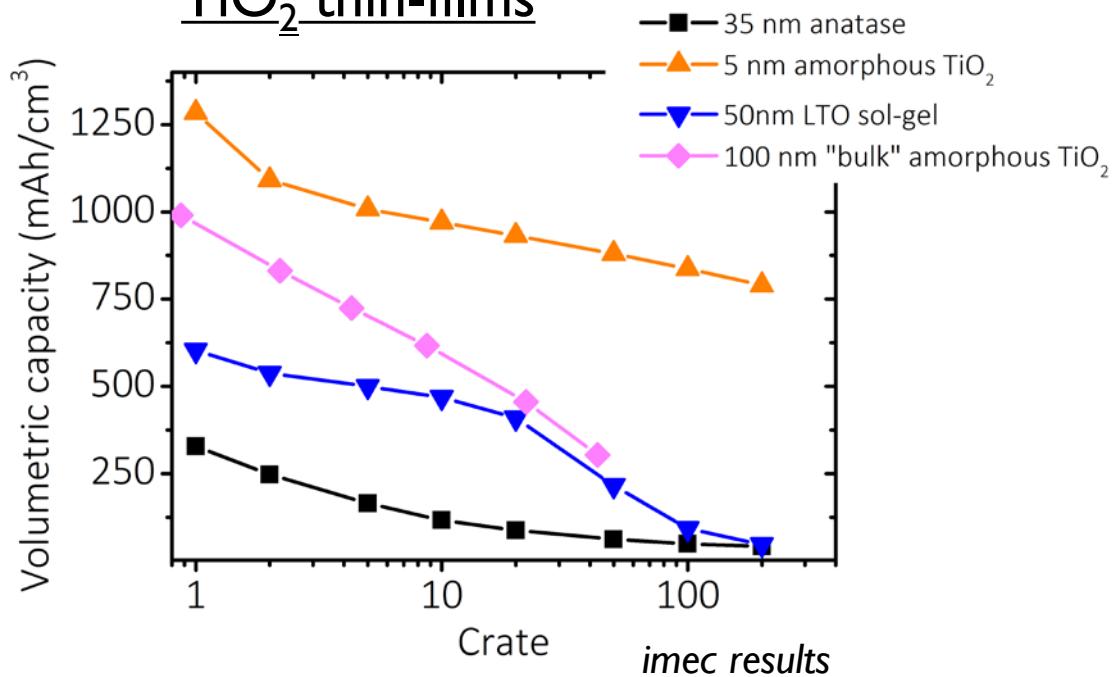
NANO-SCALING INCREASES EFFECTIVE CAPACITY

More Li-ions can be stored in truly nanoscaled materials

- ▶ Due to new stabilized phases
- ▶ Due to elimination of kinetic hindrance
- ▶ Due to mechanical stability

M. Wagemakers et al., JACS, 129(14), 4323 (2007)

TiO₂ thin-films



TiO₂ nanoparticles TU-Delft

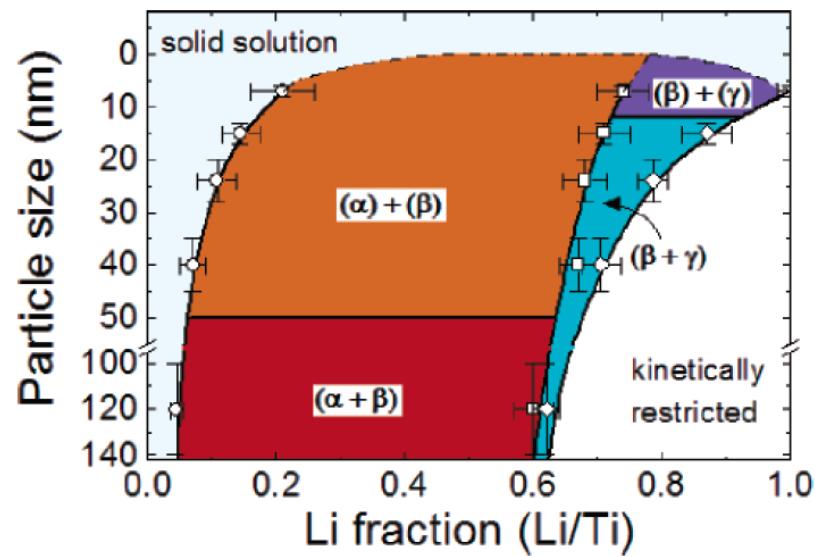
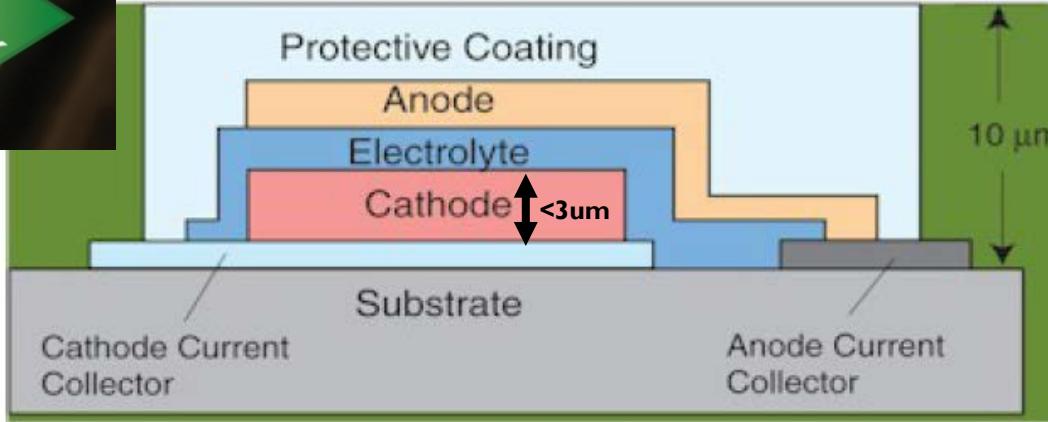


Figure 2. Phase diagram of the Li composition in anatase TiO₂ versus crystal particle size based on the neutron diffraction results. α indicates

PLANAR THIN-FILM BATTERIES HAVE LIMITED CHARGE CAPACITY



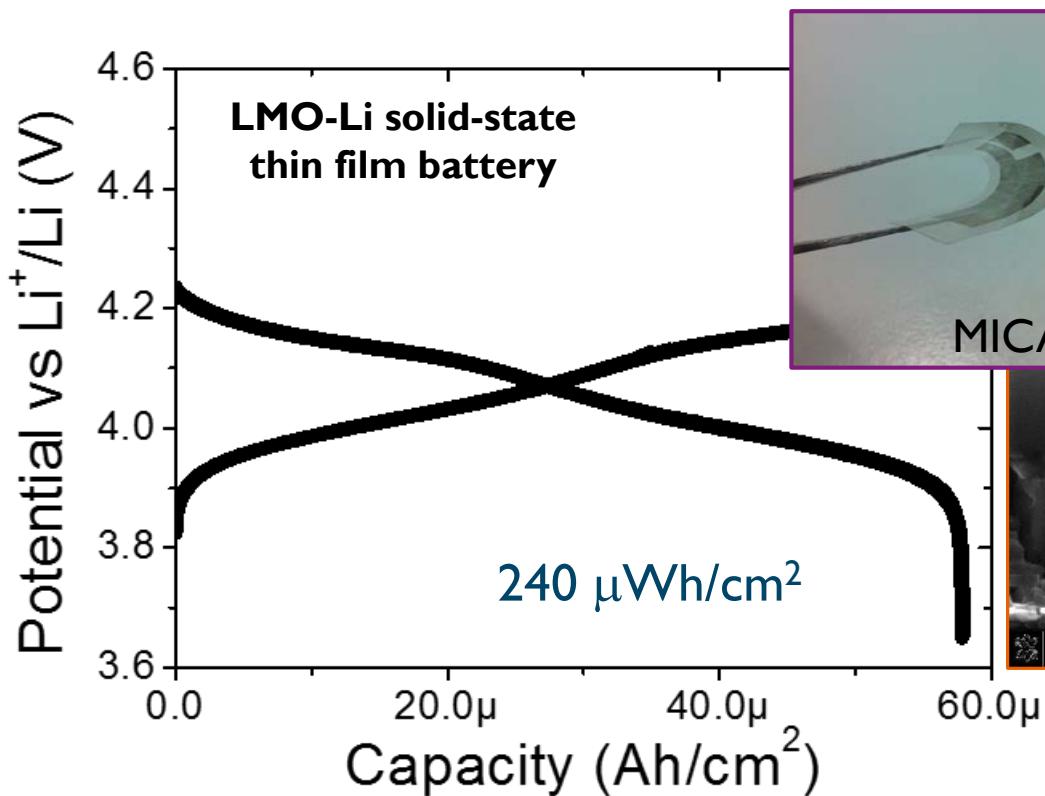
Construction of a thin-film battery. (Source: John Bates, Oak Ridge Micro-Energy).



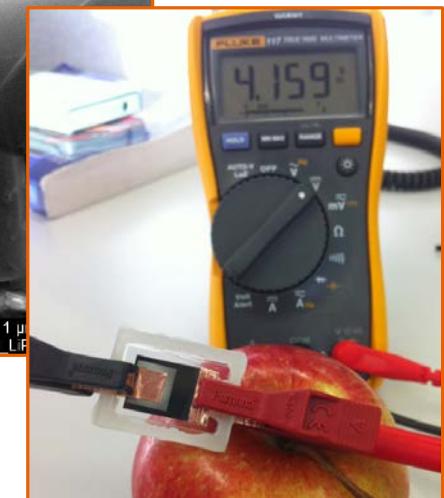
Small cells for
microstorage
only at this
point

- Thin films allow fast charging at C-rates $> 10C$ (less than 6 minutes)
- Charge Capacity is low (0.01 to 1 mAh) because of thin electrodes.
- Vacuum deposition for all layers, e.g.
 - Cathode: LiCoO₂
 - Electrolyte: LiPON glass
 - Anode: Li Metal, SnN₃

IMEC 4V PLANAR THIN-FILM BATTERY, ALSO FLEXIBLE



1 μ m LMO film has maximum theoretical capacity of 63 μ Ah/cm² (or 250 μ Wh/cm² against Li)

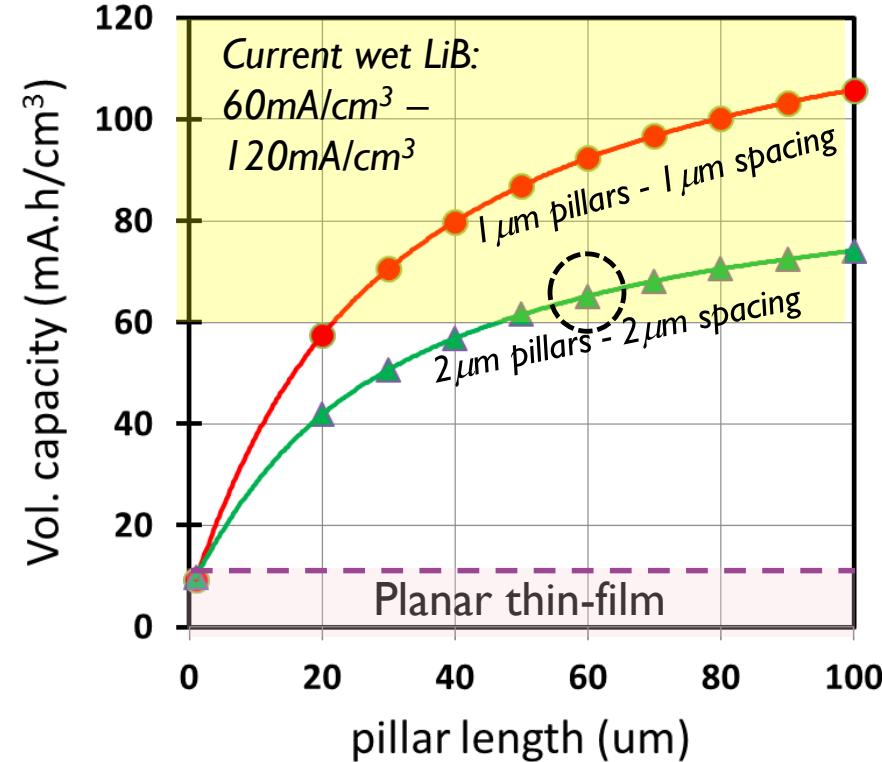
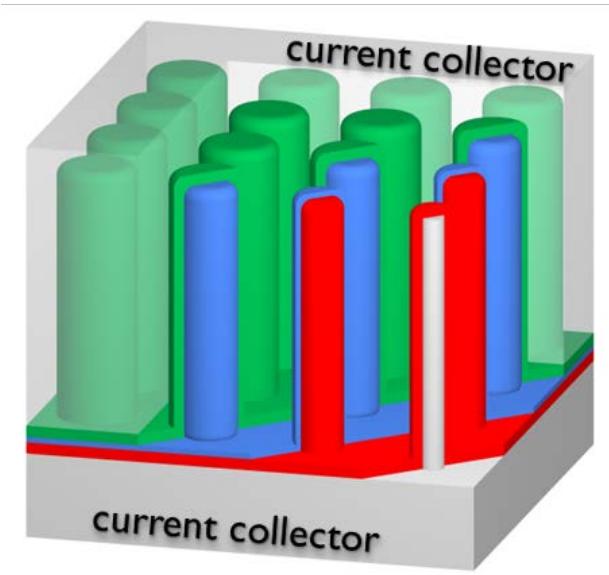


The battery stack consists of a LiMn_2O_4 cathode layer prepared by RF-sputtering and post treatment annealed, an electrolyte layer of LiPON prepared by RF-sputtering and an anode layer consisting of a lithium metal thin film prepared by thermal evaporation.

3D THIN-FILM BATTERIES FOR INCREASED CAPACITY

Goal of 3D patterning:

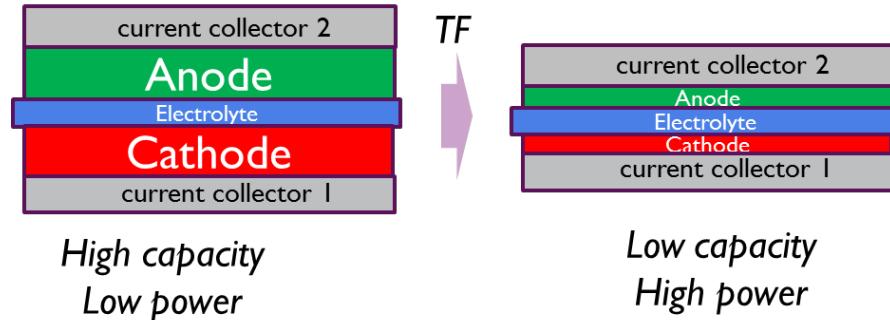
- reach the same capacity density as wet cells



THIN-FILM BATTERIES GOING TO 3D TO COMBINE HIGH SPEED + HIGH CAPACITY

High speed:

- How: Thin electrodes and electrolyte
- Target: 80% capacity at 20C (3 min charging)
compared to current 80% at 2C (30 min) wet cell

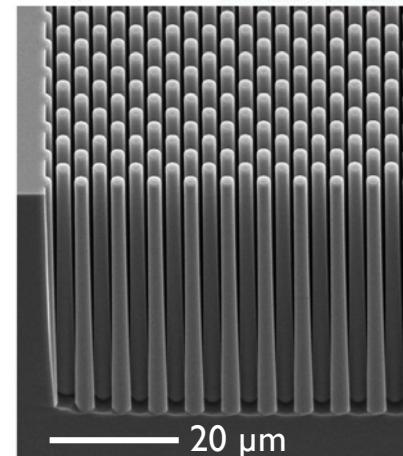
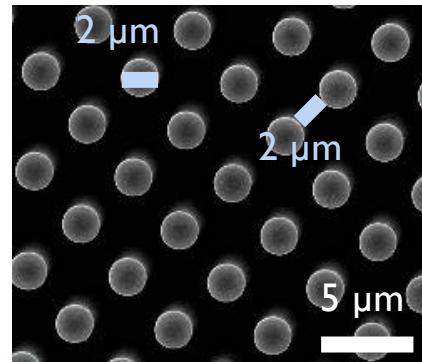
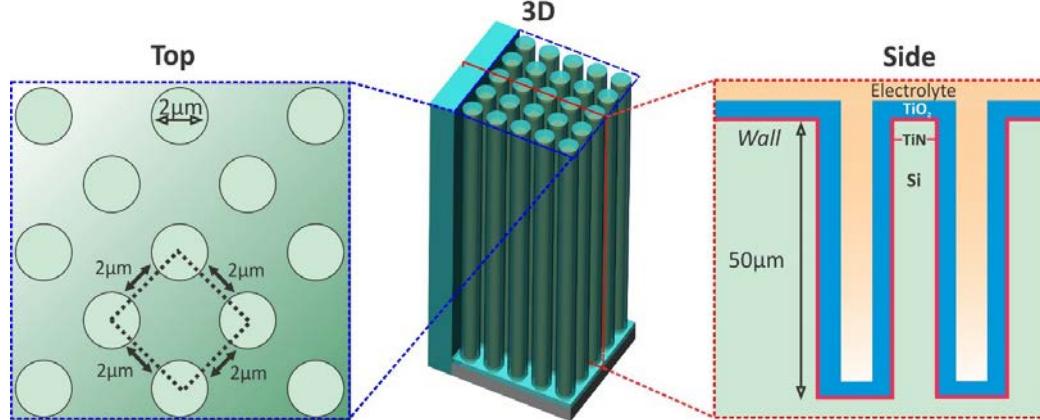
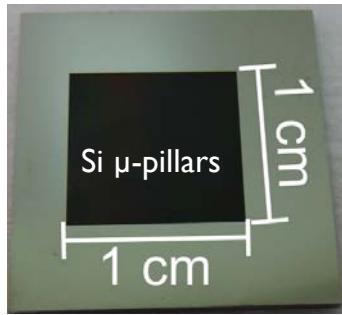


High capacity:

- How: 3D structure (micropillars)
- Target: 60-120 mAh/cm³ (in range of current wet cells)
- Status: technologies for coating ANODE and CATHODE on high aspect ratio pillars are ready
(see next slides!) – conformal electrolyte is next step

Si pillar arrays as 3D current collector substrates

- Si μ -pillars are fabricated by lithography patterning and deep reactive ion etching on 300 mm Si wafers



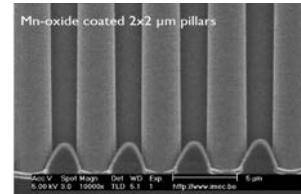
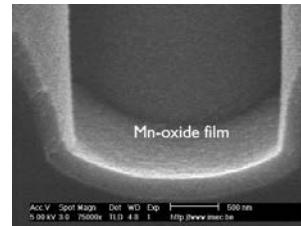
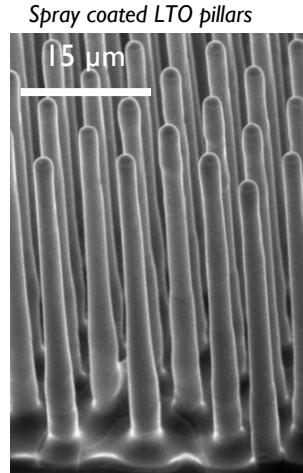
50-60 μ m high

Area
enhancement of
20-25x

Conformal Deposition Techniques

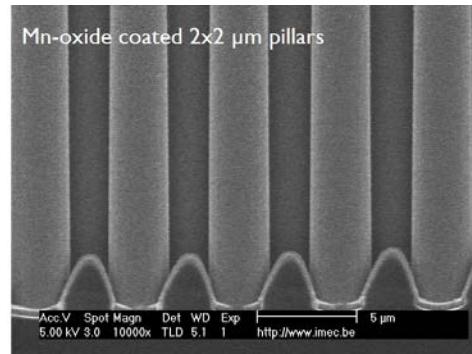
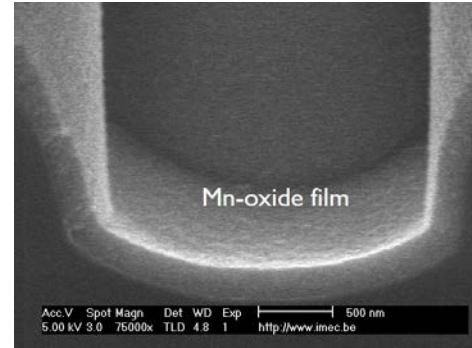
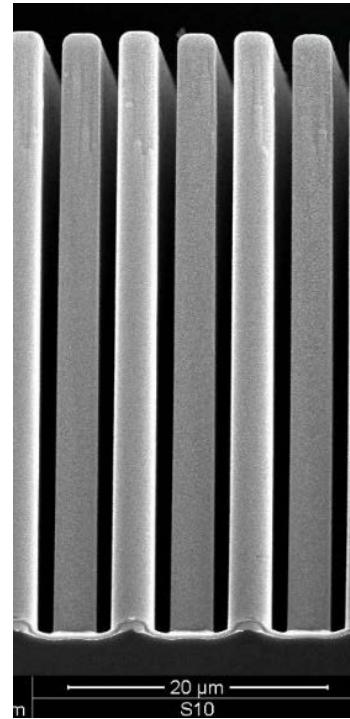
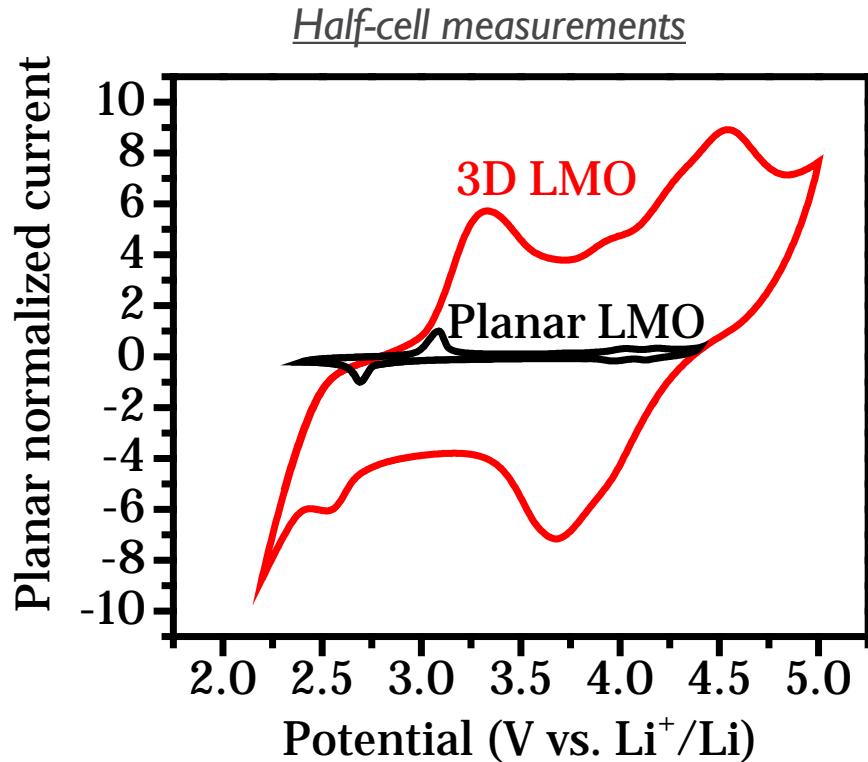
Various conformal deposition technologies developed for electrodes and electrolyte

- Electrochemical deposition (ECD) demonstrated
 - Excellent conformity of adherent films
- Chemical solution deposition (CSD) demonstrated
 - Conformal coating by spray coating demonstrated
- ALD and up-scalable spatial-ALD demonstrated
 - Good conformity at practical deposition rates



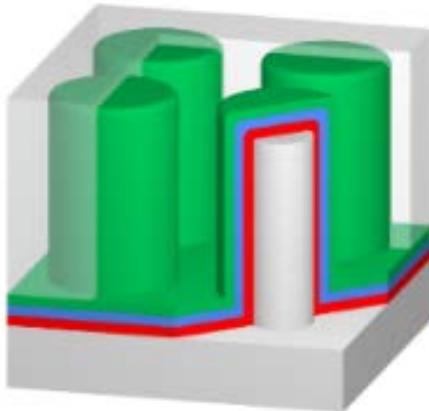
Conformal Deposition of LiMn_2O_4 Positive Electrode

Pillars of 2 μm in diameter with 2 μm spacing and 50 μm high: area enhancement of $\sim 20\times$

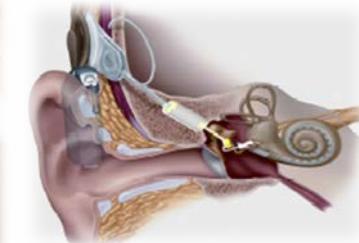
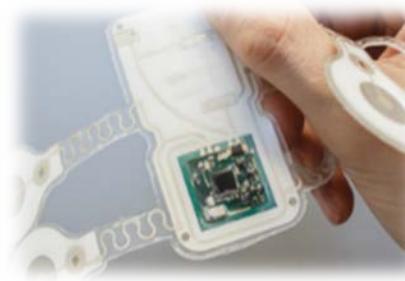
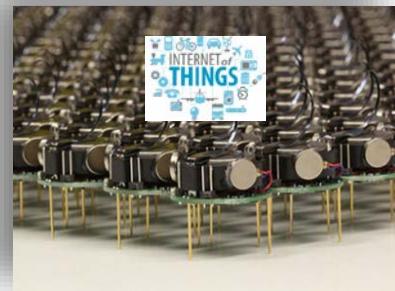


3D-TFB ENABLE INSTANT RECHARGING

- Our 3D thin film batteries enable ‘*Ultra Fast Charging*’ which is especially of interest for small electronics where space and thus battery capacity is limited and at the same time they ensure ‘Safety’, ‘long battery Life-time’ and ‘seamless Integration’ for **IoT, wearables, implants and smart electronics**



3D Thin-film battery



ASPIRE
INVENT
ACHIEVE

