Progress in the development of 3D concentric on chip lithium ion micro battery

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Acknowledgement

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Cooperation with:
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Nachum Lavi, - mechanical workshop

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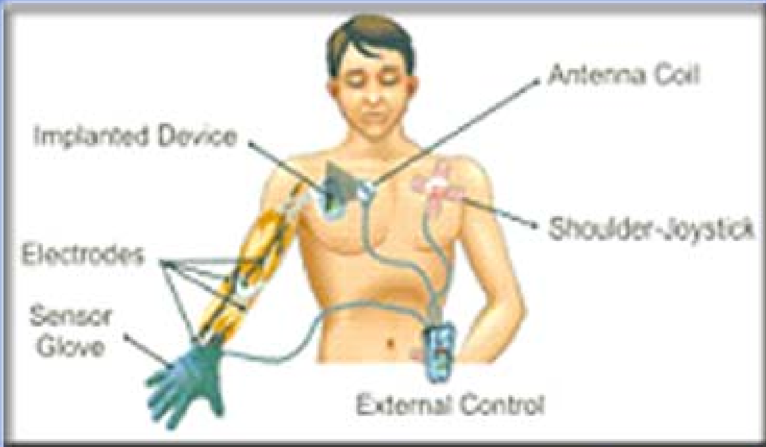
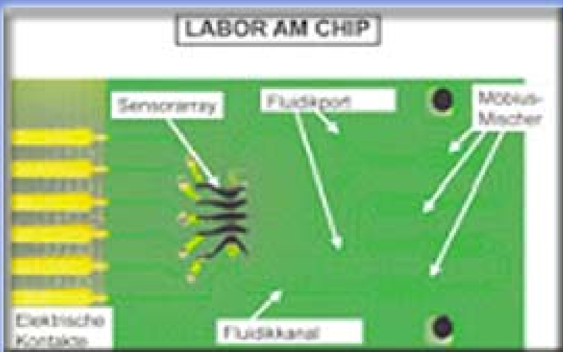
Government of Israel, RAMOT – (University Authority for Applied Research and Industrial Development Ltd)


Antenna Coil
Implanted Device
Shoulder-Joystick
Electrodes
Sensor
Glove
External Control



LABOR AM CHIP
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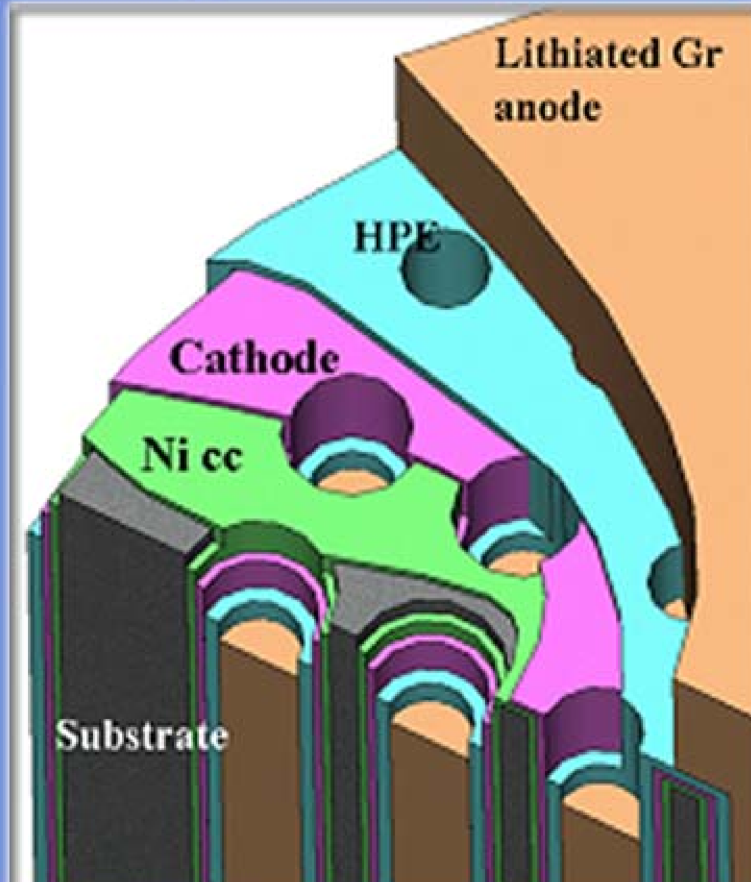
Möbius-
Mischer
Elektrische
Kontakte
Fluidikkanal

Lithiated Gr
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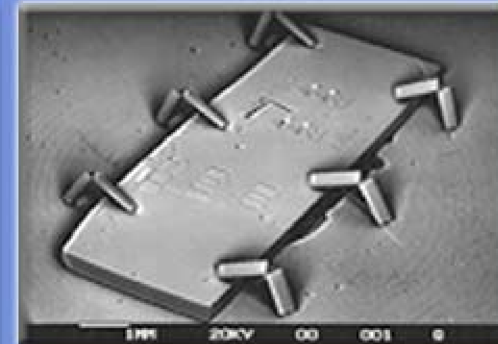
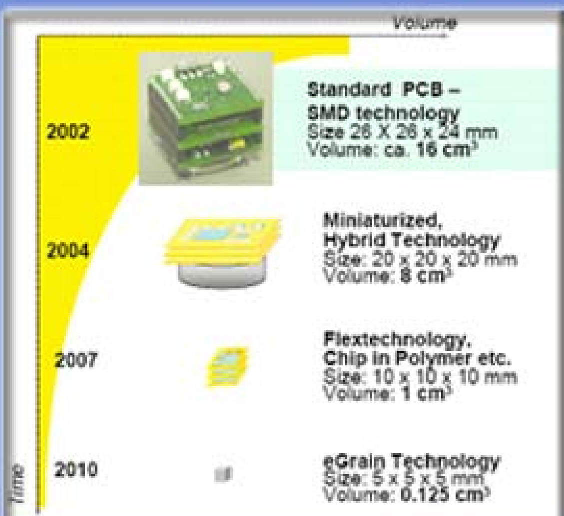


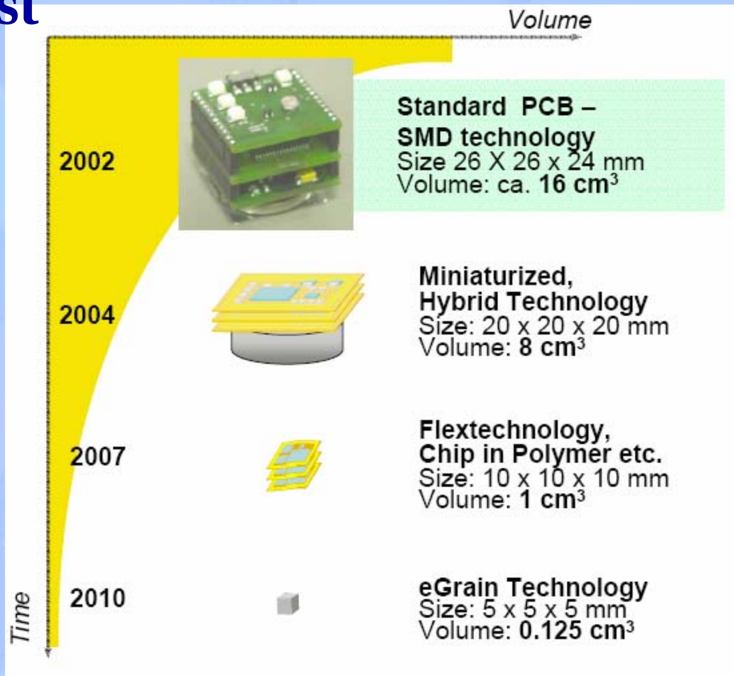


Volume
Time
2002
Standard PCB –
SMD technology
Size 26 X 26 x 24 mm
Volume: ca. 16 cm³
2004
Miniaturized,
Hybrid Technology
Size: 20 x 20 x 20 mm
Volume: 8 cm³
2007
Flextechnology,
Chip in Polymer etc.
Size: 10 x 10 x 10 mm
Volume: 1 cm³
2010
eGrain Technology
Size: 5 x 5 x 5 mm
Volume: 0.125 cm³

Outline

- The motivation for developing 3DMB (10μAh-10mAh)
- 2D lithium ion micro battery
- Cathodes for different applications will be demonstrated. 1.5-2V; 3-4V cells.
- Performance of TAU 3DMBs.
- Summary

MB requirements for μ - power sources applications

- ➢High integrity containment & minimum size
- ➢SAFETY – especially when used in in vivo applications
- ➢Long-term Energy Supply in MEMS; need High Power Level
- ➢Rechargeability
- ➢Produceability in large quantity and low cost



Fundamental problem of 2D-MBs:

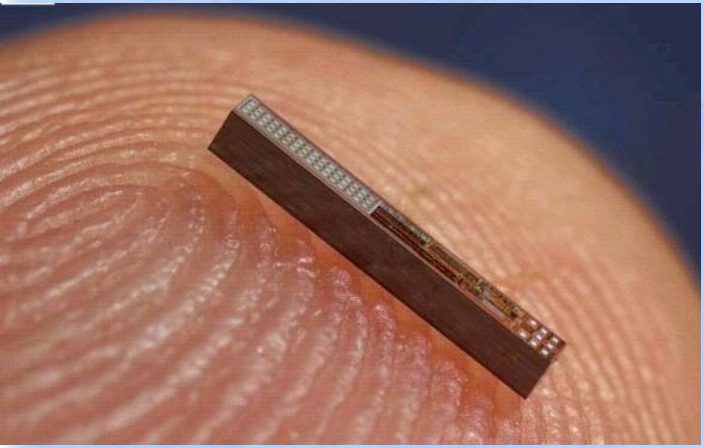
limited foot print area →

limited active electrode surface area

Sensor in Artery Measures Blood Pressure

ScienceDaily (Jan. 19, 2009)

Fraunhofer researchers; Dr. Osypka GmbH



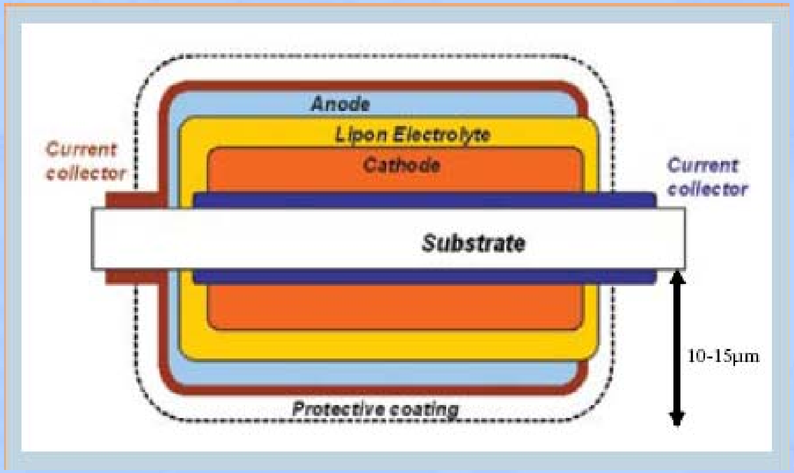
Diameter~1mm including its casing
Power - wirelessly via coils

The smallest battery on the market is a 4.7mm (diameter) coin cell (Varta, Seiko)

There is a need for a powerful, mm and sub-mm battery size,
The device can be implanted using a syringe needle or take very small volume

http://www.sciencedaily.com/releases/2009/01/090119081512.htm

Thin-film batteries
the most advanced of LiBat systems



Based on:J.B. Bate, SSI *135 (2000)*

	Typical performance
Voltage [V]	2-4
Capacity [μAh/mm^2]	1-3
Energy [μWh/mm^2]	2.5-10
Power [μW/mm^2]	4 - 70

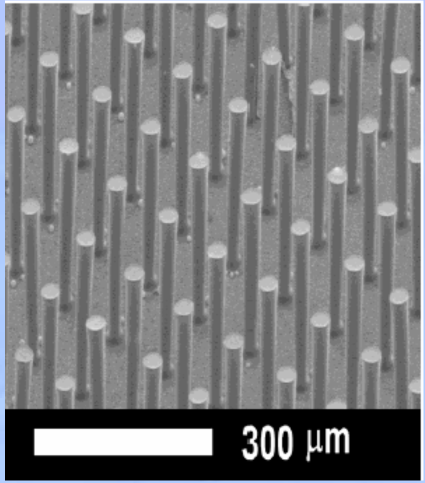
U.S companies have licensed Thin-film MB ORNL tech:

Bordeaux Univ.& Hydromech.(HEF)1,
Eveready Battery Co.1
Front edge technology inc.,
LiTE Star
Oakridge Lab.2,
Cymbet inc.,
Excellatron solid state Inc.

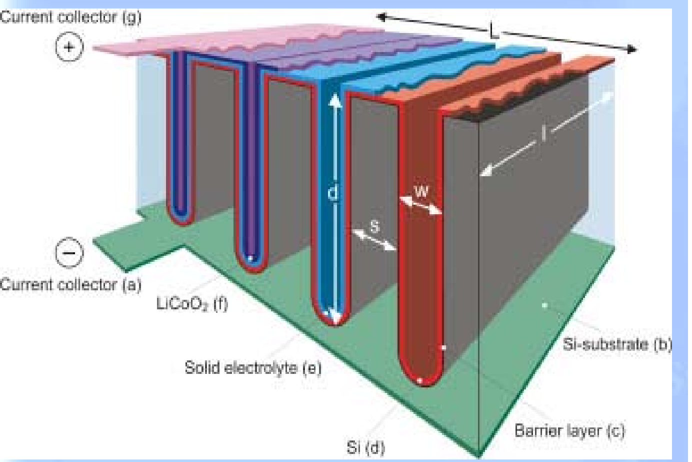
3DMB architecture under development

- Perforated Si (TAU)
- Interlaced Si (TAU)
- Etched trenches in Si (Notten)
- Post-electrode-array structures

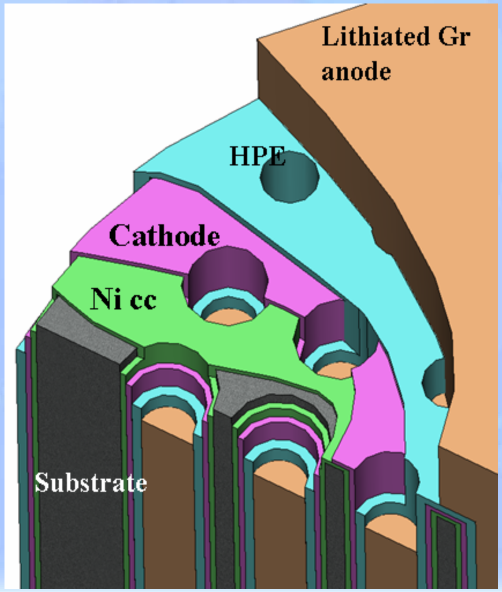
(Madou, Dunn, Tarascon, Thomas)

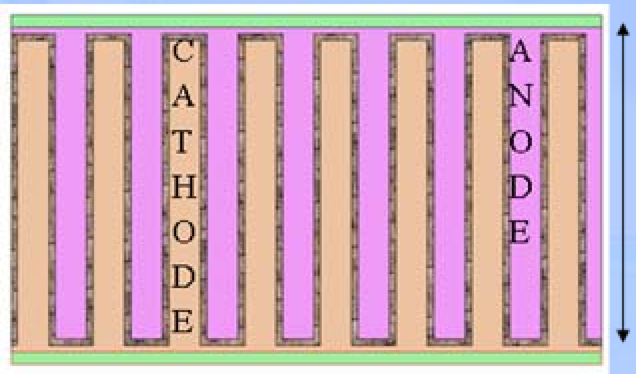


(M. Madou, *ESSL*, 7, 2004)



Peter H. L. Notten et. al.
Adv. Func. Mat. 2008

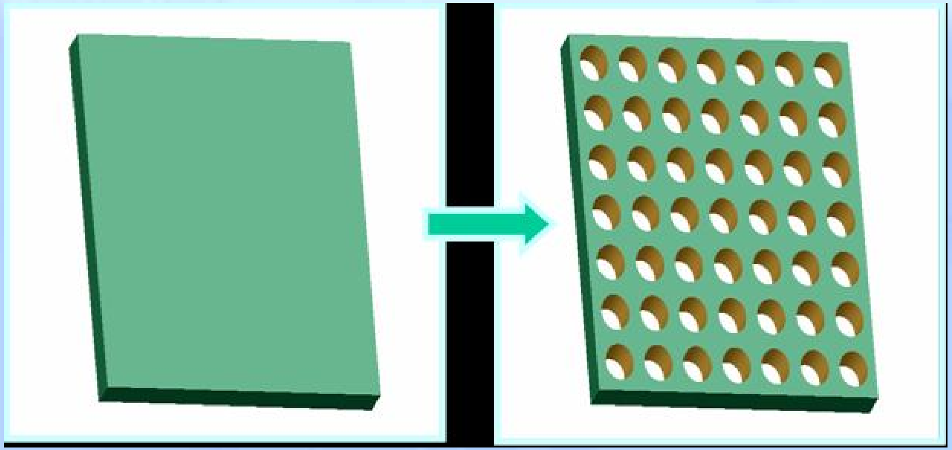


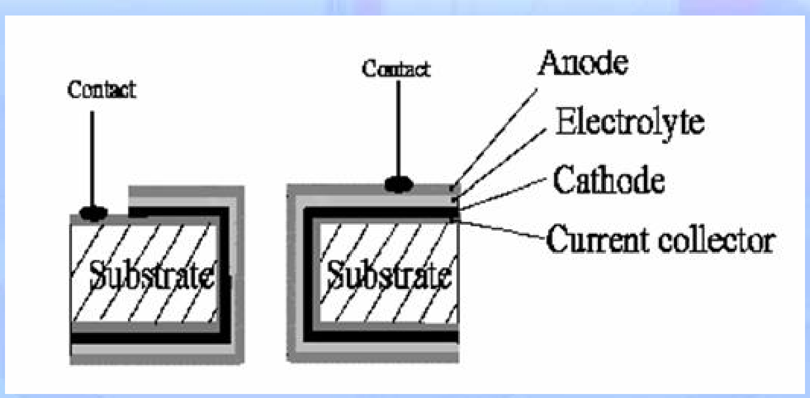


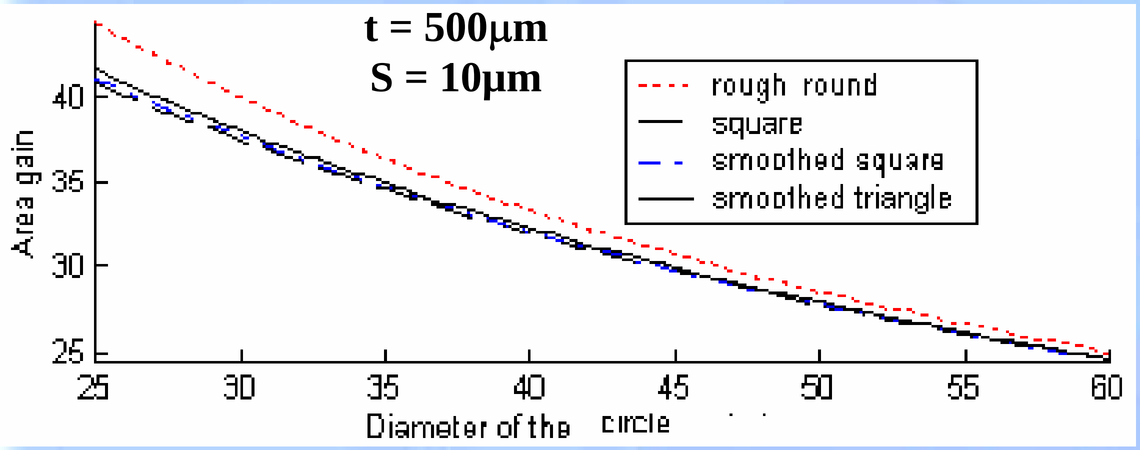
The benefits of using the TAU type 3DMB configurations

- **Higher energy and power per a foot print (using a thin separator, it keeps ion transport distances short).**
- **Utilize the dead (unused) volume of the substrate or the chip.**
- **Mechanically more rigid than the post type 3DMB.**
- **The use of perforated or interlaced configuration provides enhanced safety (especially for high power batteries)**

Perforated substrates with high-aspect-ratio holes







$$A.G. = \frac{\pi d}{(d+s)^2}\left(t - \frac{d}{2}\right) + 2$$

Dimensions:

t- substrate thickness

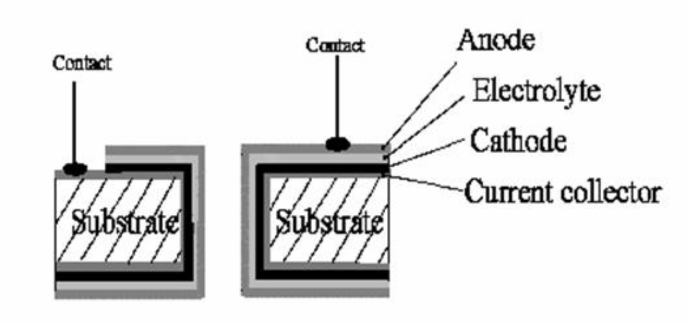
d- holes diameter

S- Inter-hole distance

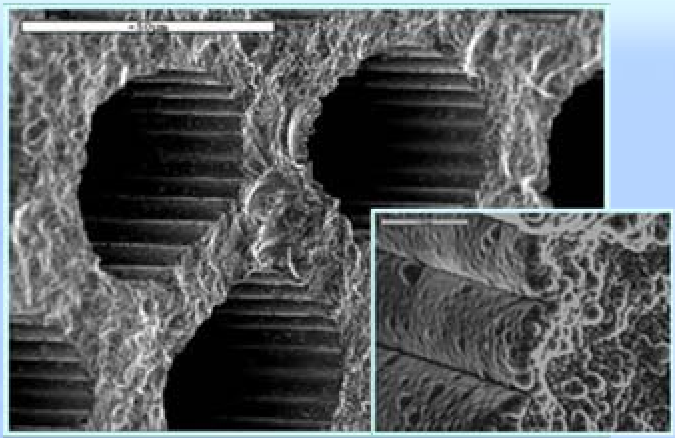
3DMB sequential fabrication stages

1. Preparation of high-aspect-ratio perforated silicon by the ICP method (20,000 cells per cm^2) .
2. Surface pretreatment of sidewalls
3. Electroless deposition of current collector
4. Electrodeposition of a thin-film cathode (few microns thick)
5. Hybrid polymer electrolyte coating (few microns thick)
6. Filling of the remain volume of holes by graphite based anode Mounting
7. of lithium foil at the top of the conformally coated perforated substrate.
8. Charging of the cell by electrolyte ($LiPF_6$, EC-DEC) and packing (in coin cells)
9. Performance tests of the 3D-microbattery

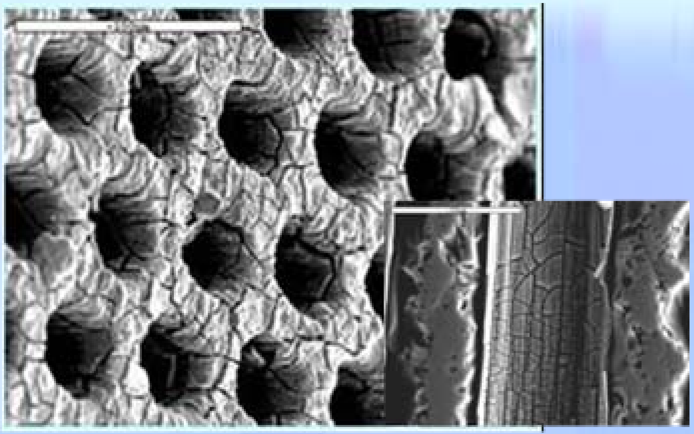
Characterization by SEM, AFM, XRD, XPS, TOFSIMS and electrochemical methods



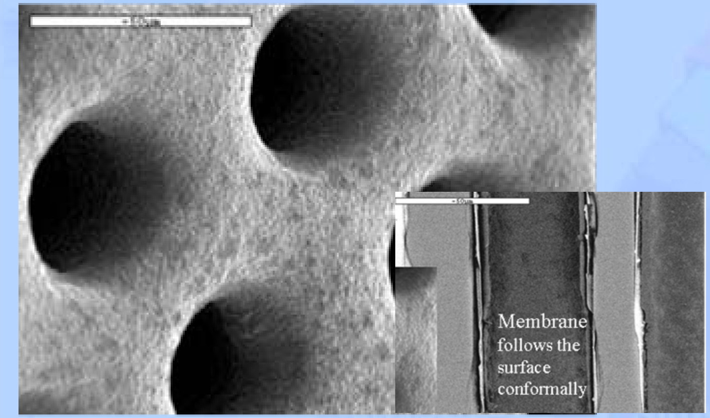
Feasibility of 3D concentric microbattery fabrication



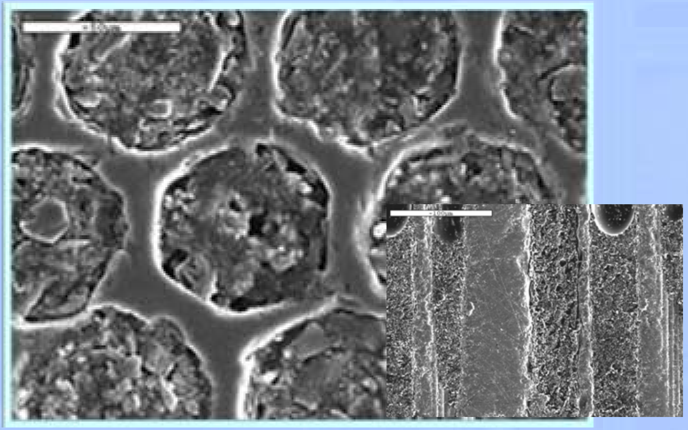
Electroless depostion of Ni current collector



Electrodeposited Cathode



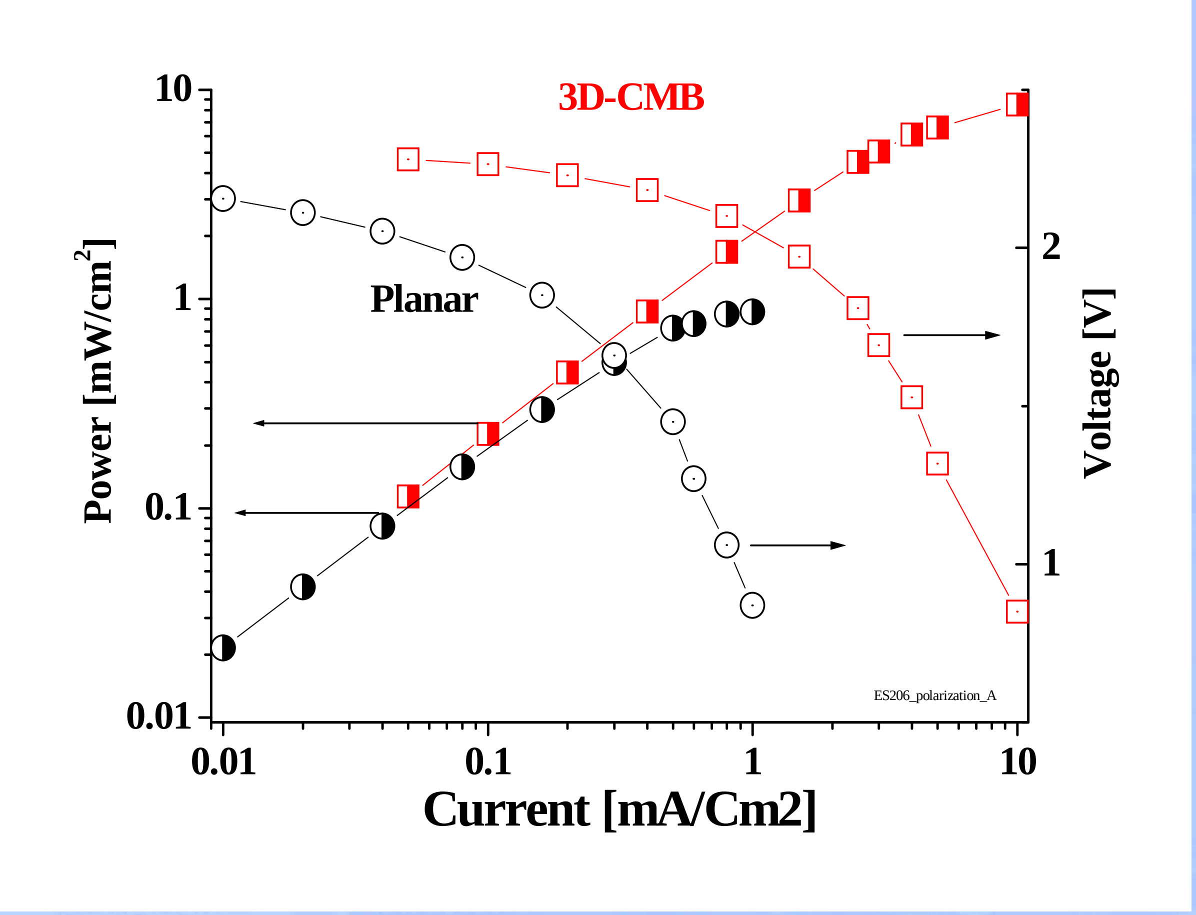
Conformal Membrane coating



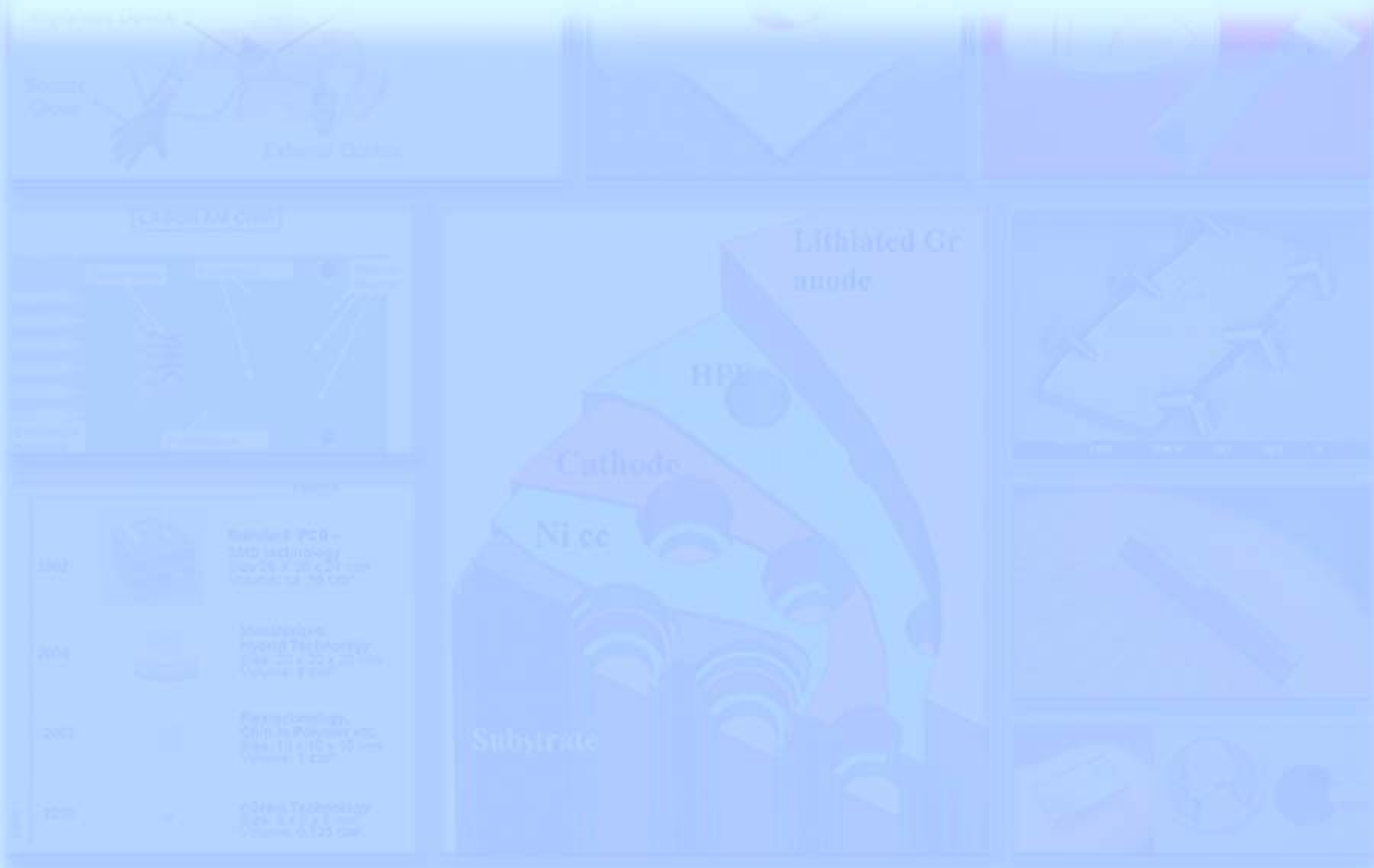
Filled Graphite anode

An order of magnitude power gain of perforated Si 3DMB

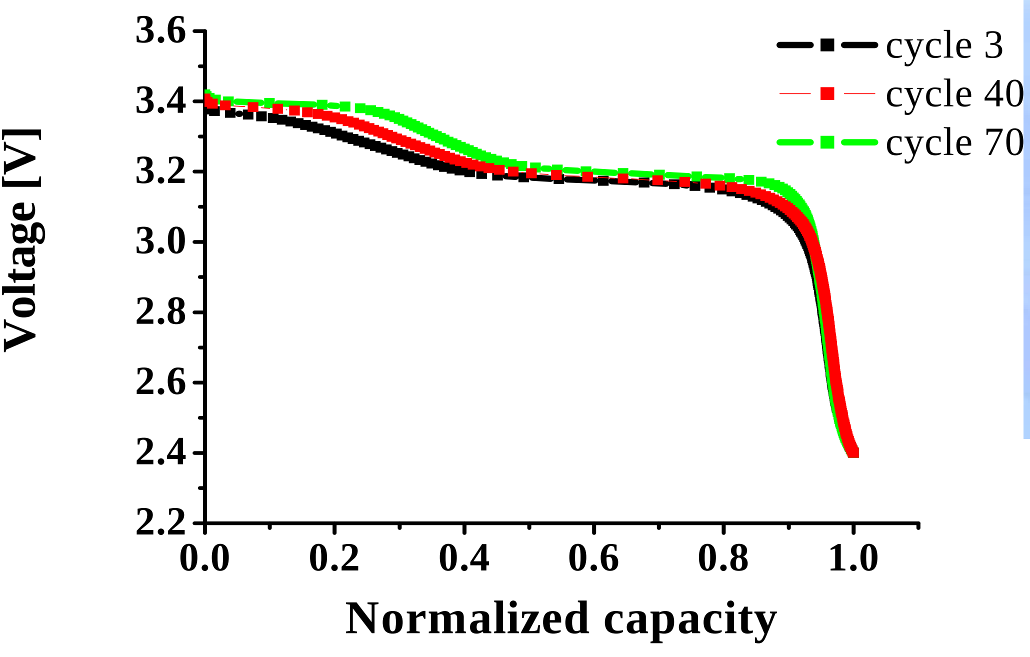
2D Vs. 3DMB – MoO_xS_y cathode and an improved anode

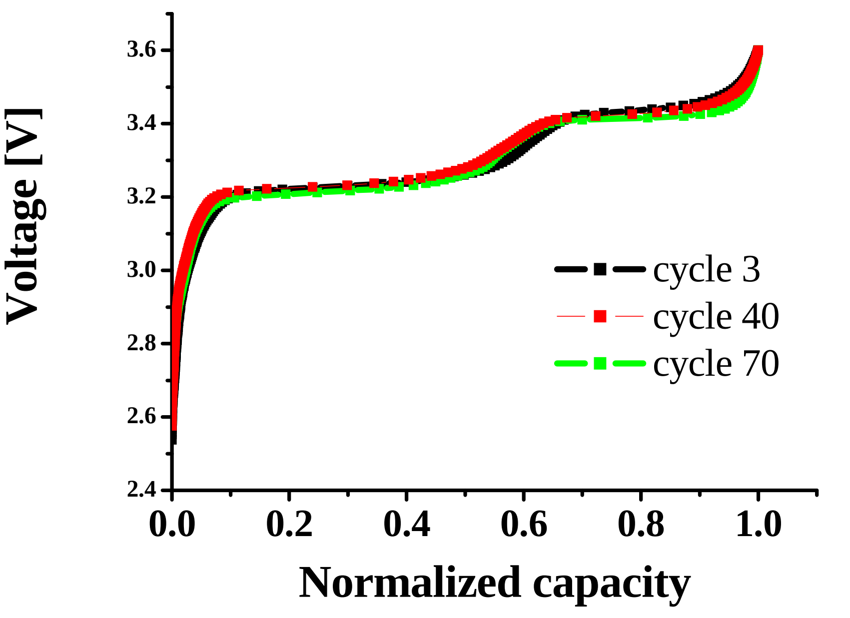


Electrodeposited Thin V_2O_5 Cathode



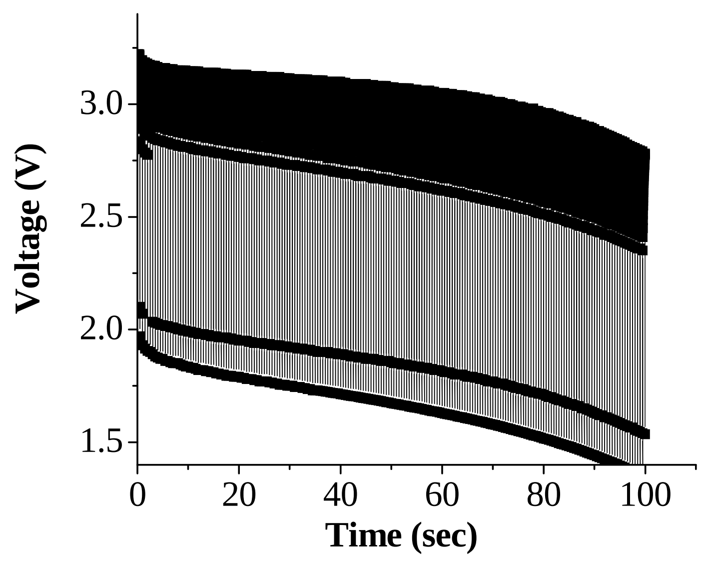
Electrodeposited 2D thin V_2O_5 cathodes

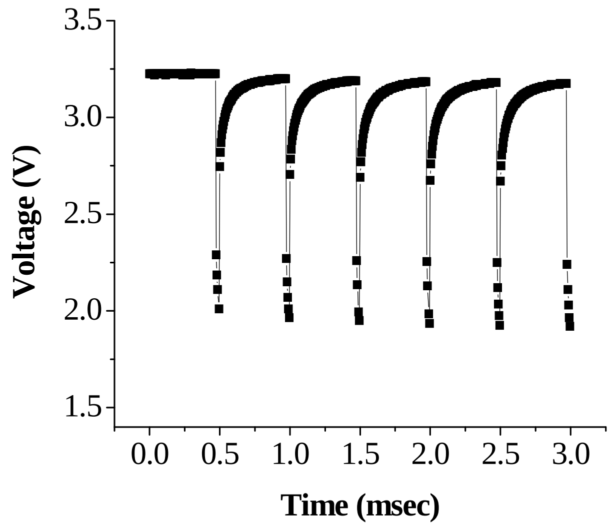


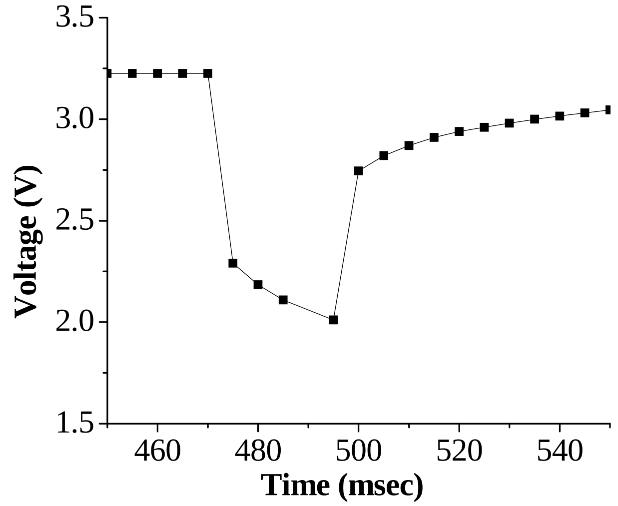


Charge - discharge curves for 2D Li-crystalline V_2O_5 cell (V-6)

High power pulse capability of lithium - V2O5 cells







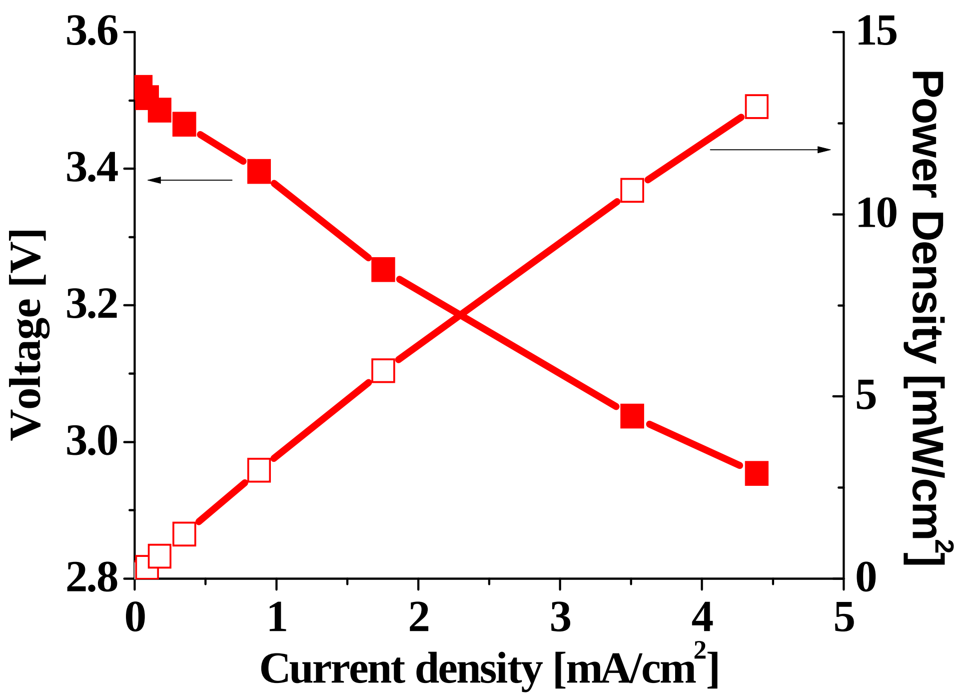
200 Pulses of 28mA/cm^2

Pulse length: 25 ms

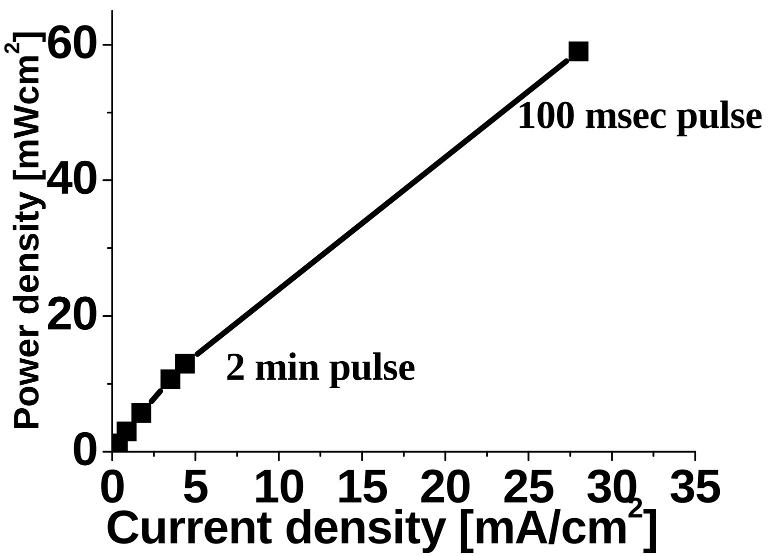
rest duration 475 ms

Average power ~59 mW/cm^2

V/I and P /I curves for Li / 2D thin V_2O_5 modified cathode



In 3D configuration (AG=25)
it is equivalent to
350 mW/cm^2 or 7W/ml)

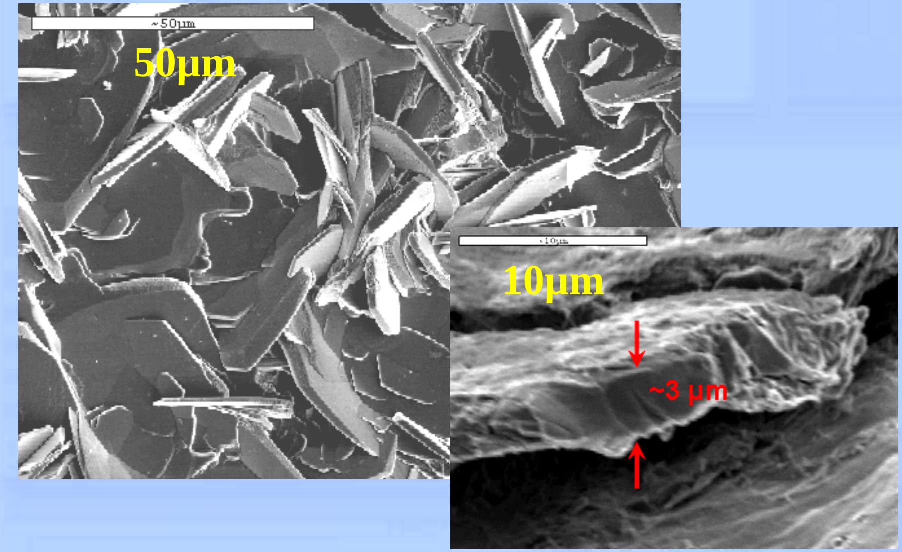


In 3D configuration (AG=25)
it is equivalent to
1470mW/cm^2 or 30W/ml)

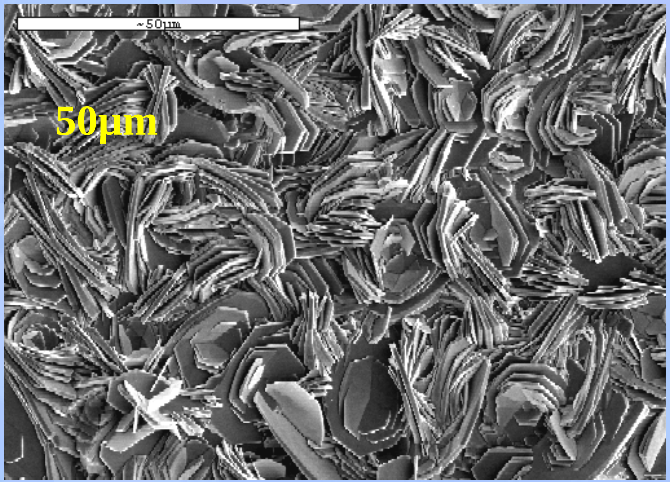
Assuming good anode; excluding packaging

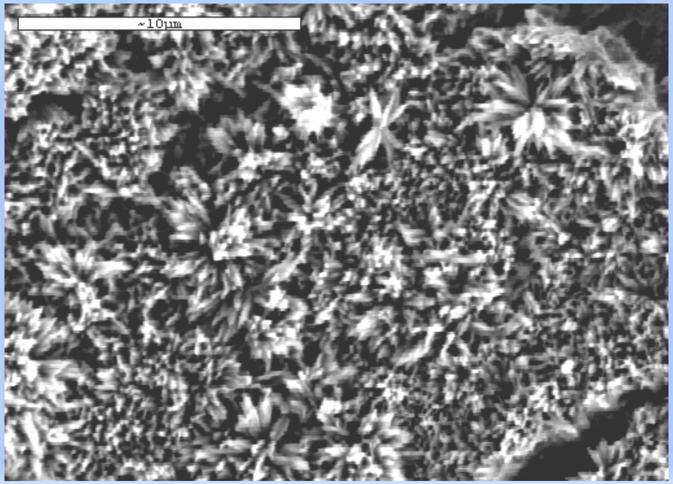
Surface morphology characterization of V_2O_5 cathodes with/without additives

V-1 1mA 1 hour



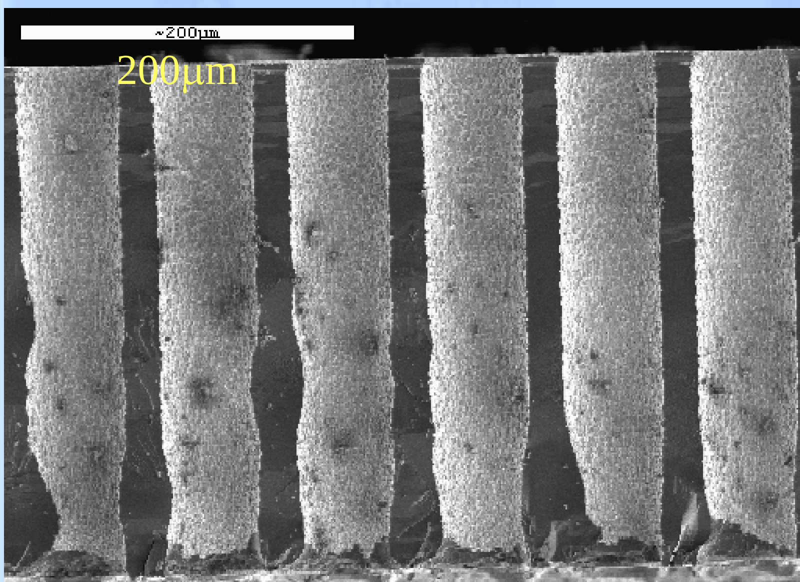
V-2 30 min 5 mA + 30 min 1 mA

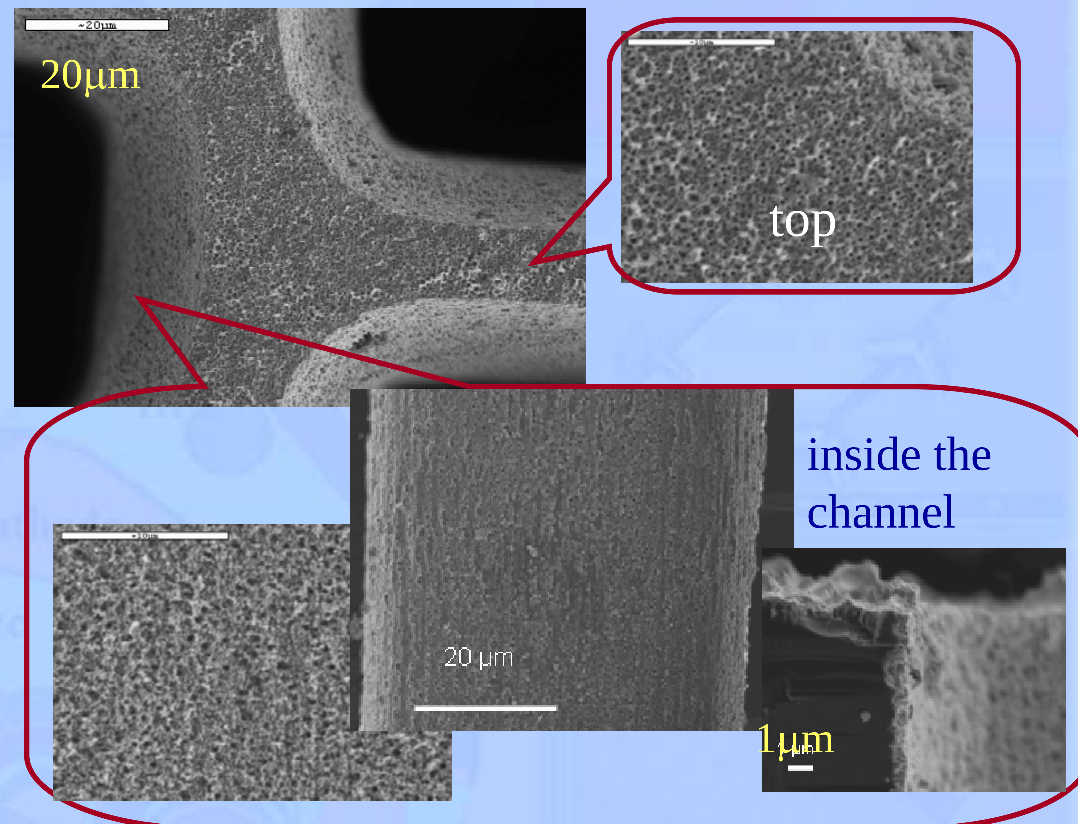




Modified cathode

Electrodeposited non-modified V_2O_5 on-3D-Si substrate

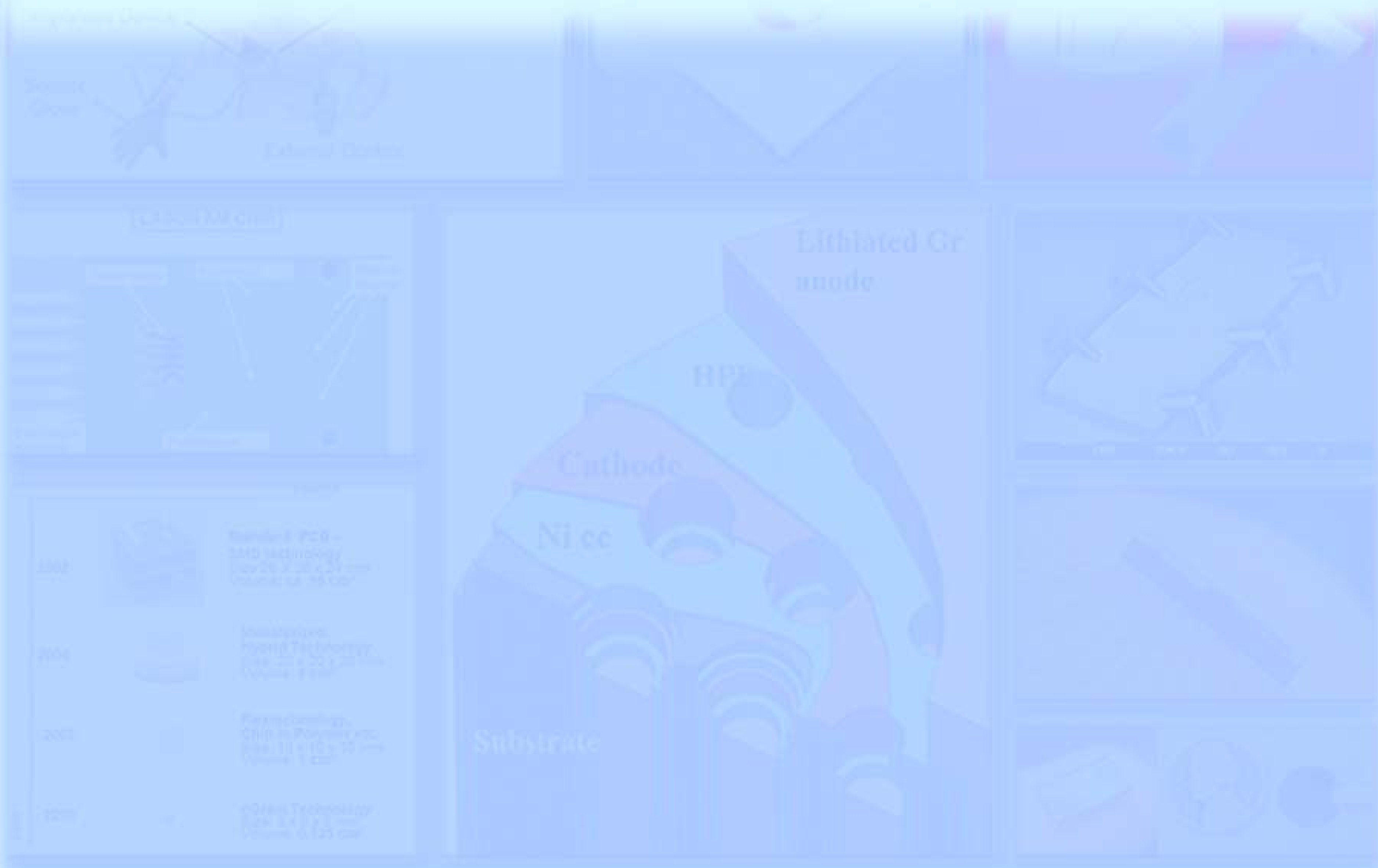




Bath composition: 0.1 M NH_4VO_3, pH=7.0, 50°C, i= 3mA/cm^2

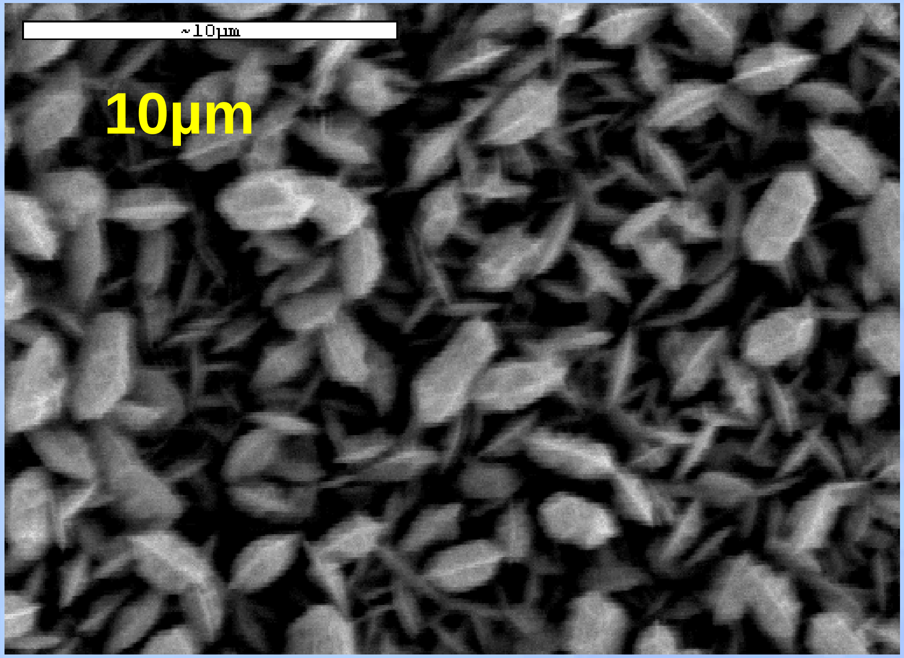
$$NH_4VO_3 \xrightarrow{pH\,2-3} NH_4V_3O_8 \cdot 0.5H_2O \xrightarrow[treatment]{thermal} 1.5V_2O_5 + NH_3 + H_2O$$

Electrodeposited thin Cu_xS_y cathode

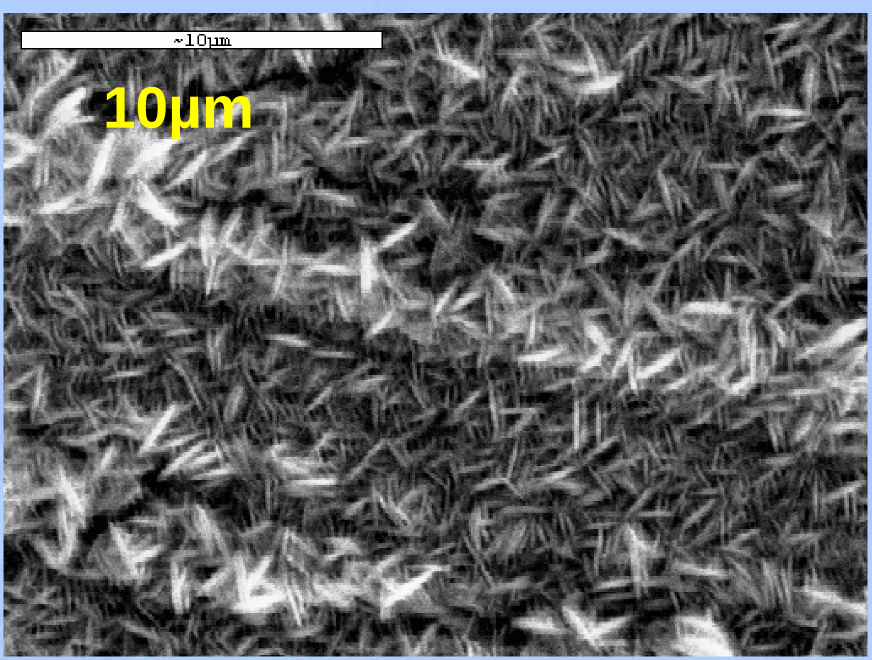


Surface morphology characterization of CuS cathodes with additives

Need a few microns or preferably sub-microns size particles

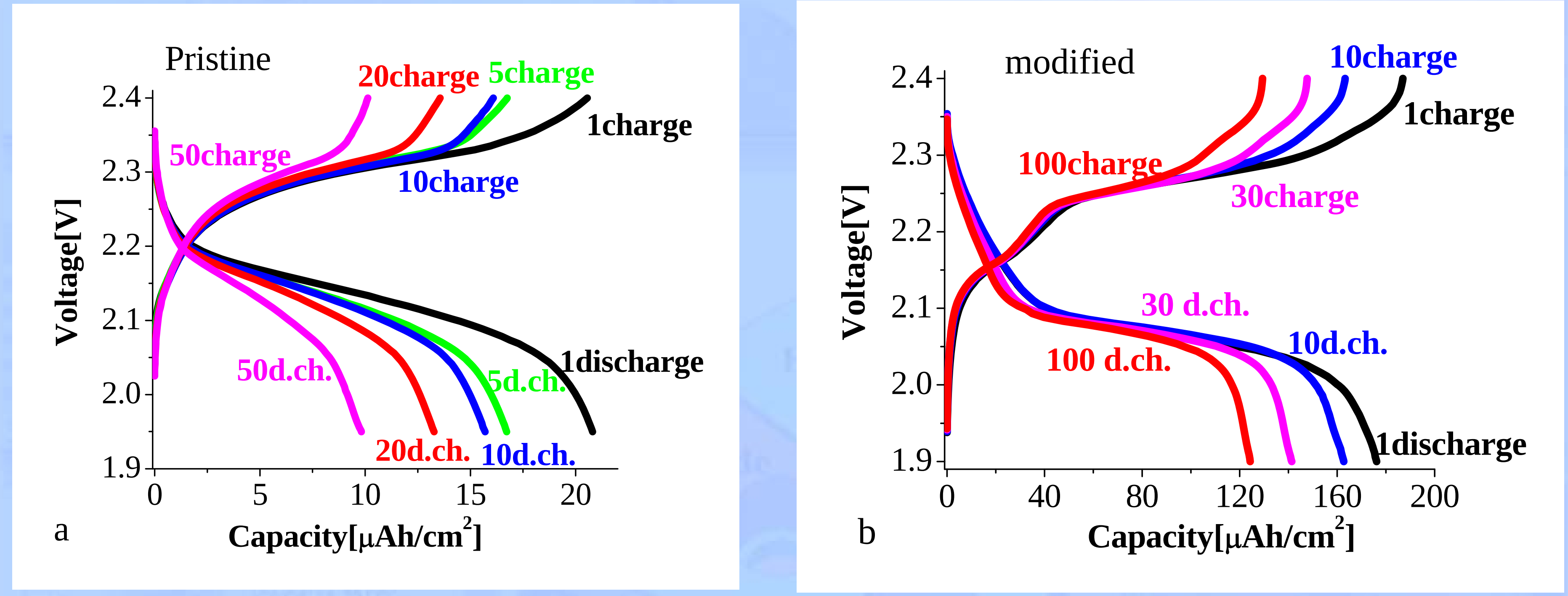


Addition of polymer to deposition bath. Not stirred



Addition of Polymer to deposition bath. Stirred

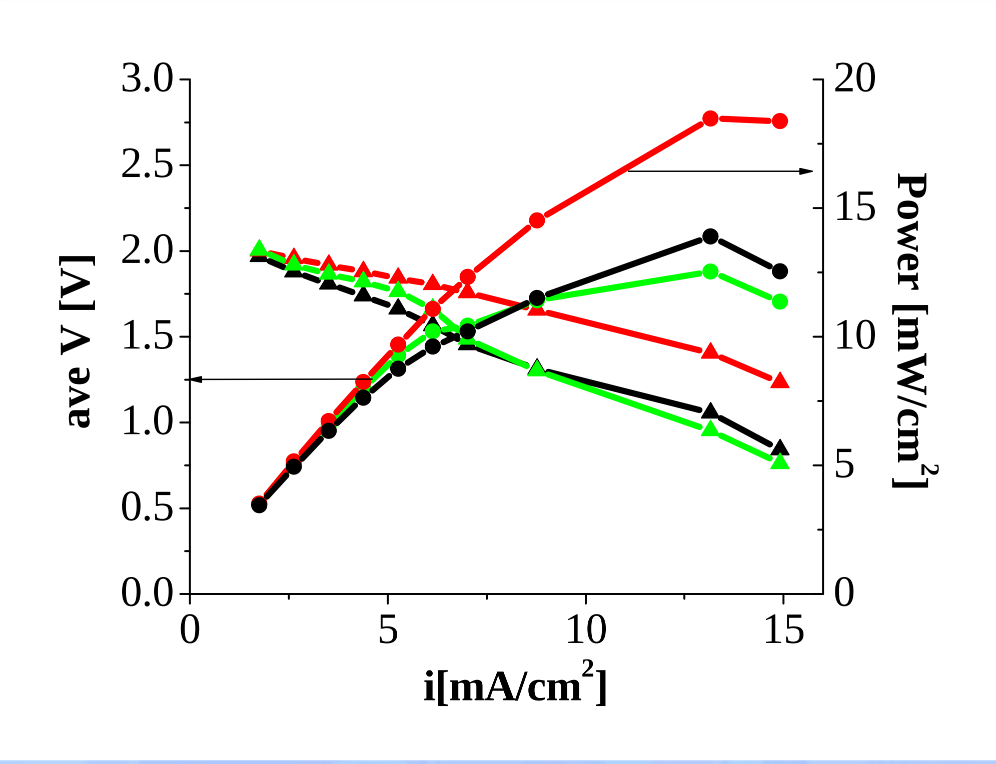
Voltage Profile of Li/Cu_xS_y cells



The discharge reaction consists of one plateau at about 2V.
The charge is a complex multi phases process.

V/I and P /I curves for Li / 2D thin modified CuS cathode

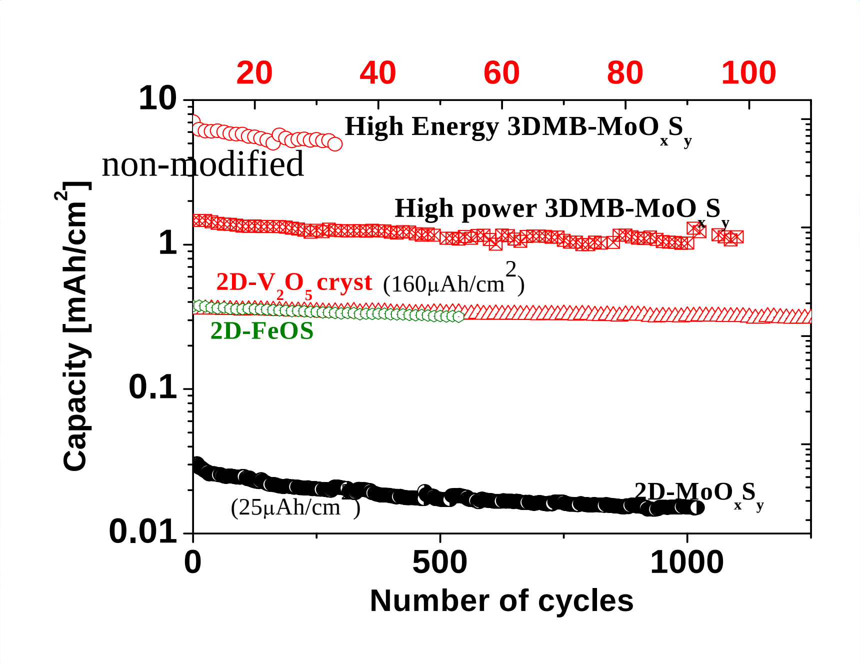
Cus49- 30min deposition time
Cus51- 40min deposition time
Cus52- 45min deposition time

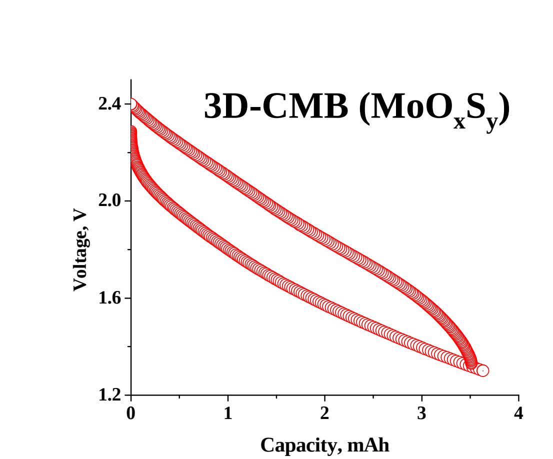


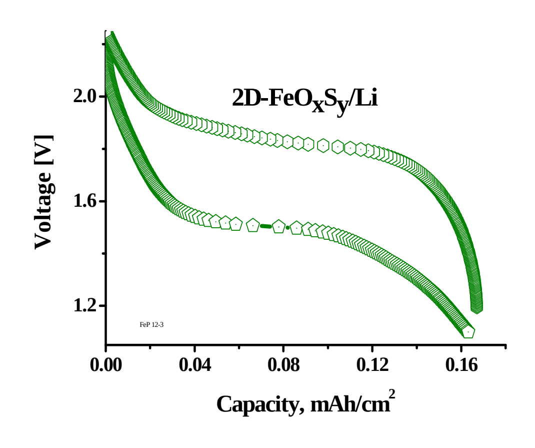
In 3D configuration (AG=25) it is equivalent to 450 mW/cm^2 or 9 W/ml)

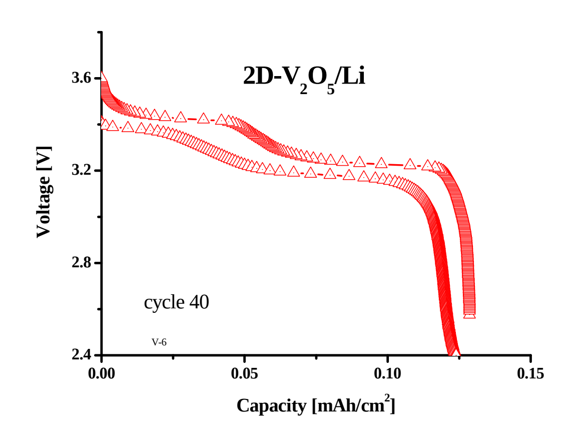
Assuming good anode; excluding packaging

Cycle life of planar and 3D-CMBs









TAU - 3DMB present and future performance

	Operating Voltage [V]	Capacity [μAh/mm²]	Energy [μWh/mm²] (mWh/ml)**	Power [μW/mm²] (mW/ml)**
Typical 2D microbattery	2-4	1-3	2.5-10	7-70
TAU-Present High-energy configuration, Thickness-0.5mm	1.7	100	170 (340)	20-200* (40-400*)
TAU-Future High-power configuration, Thickness-0.5mm	1.7-3.4	40-60	120-180 (240-360)	500-4500* (1000-9000*)

* pulse, ** excluding package, assuming a good anode

Summary

- Microbatteries have many medical and technological applications. They started to make their first step into the market.

- An increase of a factor of 25 in energy and a factor of 10 in power per a foot print was demonstrated by the 1.7V Li ion – MoO_xS_y 3DMB.

- These 3DMBs demonstrated 100 charge discharge cycles and a power density of 400 mW/ml (10 sec pulse, excluding packaging).

- Procedures for high aspect ratio, electro-deposition process of several thin 1.7 to 3.4V cathodes (including: CuS, FeO_xS_y, V_2O_5, and MoO_xS_y) were developed.

Summary

• High-power lithium ion 3DMB, based on CuS and V_2O_5 cathodes are expected to have over 240 mWh/ml and up to 9000 mW/ml (10 sec pulse, excluding package, assuming a good anode).

• High power 3D Li ion batteries based on perforated Si (or other substrate) are expected to be safer than the ordinary batteries and that based on an electrode post array

Acknowledgement

Team members:
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Rest of team members

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