Ultrashort pulsed laser ablation for decollation of solid state lithium ion batteries

Patrick Gretzki – LSE 2019

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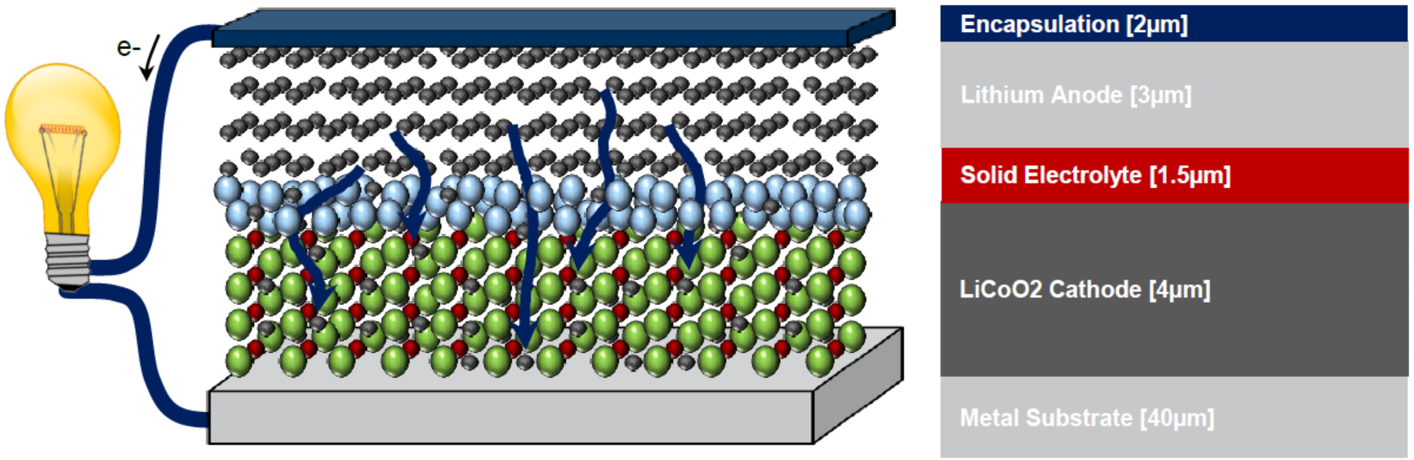
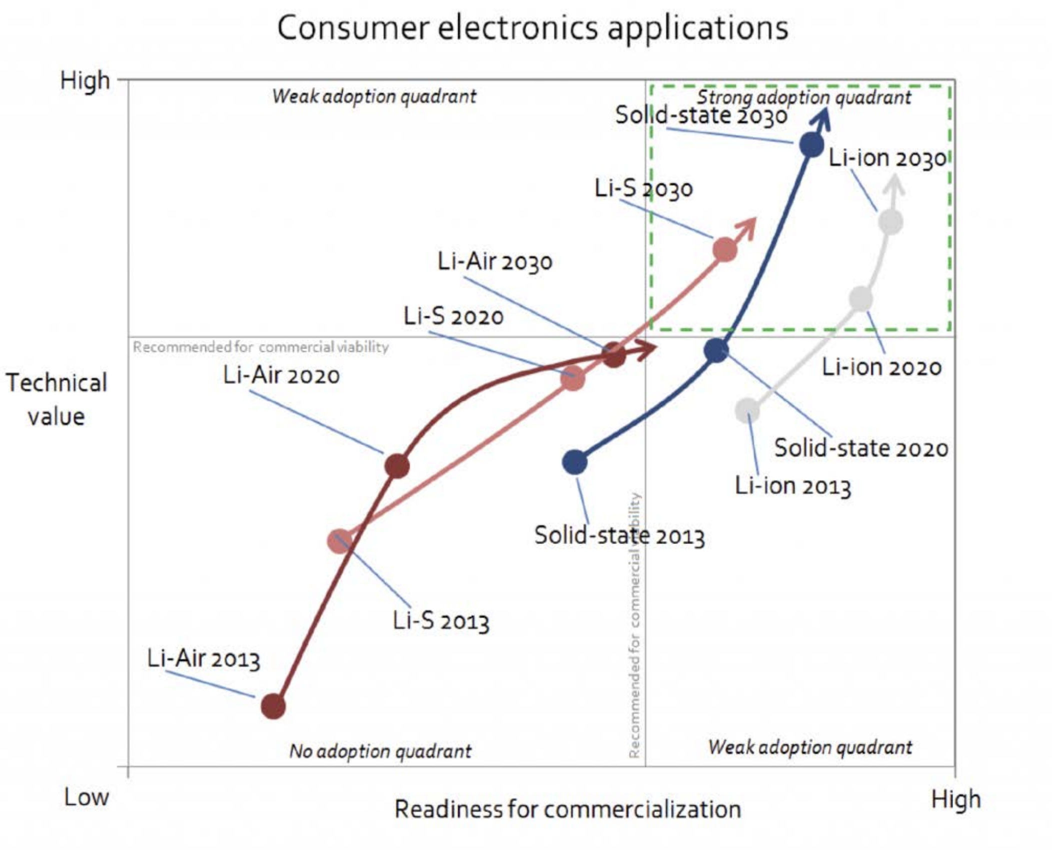
ILT

Solid state lithium batteries
Overview

- Many applications require high energy density
  - Mobile computing, IoT, power tools, electro-mobility
- Solid state electrolyte
  - $Li_7La_3Zr_2O_{12}$ (LLZ) / $Li_{10}GeP_2S_{12}$ (LGPS)





Source: Lux Research, Inc.
www.luxresearchinc.com

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Solid state lithium batteries
Advantages

- **High energy density**
  70% better in volumetric energy density
- **Safety**
  No liquid electrolyte
- **Long cycle life**
  more then 1000 full cycles (23000 cycles target)
- **Wide operation window**
  Temperature range -20°C..60°C (peak 150°C)
- **High discharge rates**
  Quick charge with 50C
- **Low self-discharge**
  only 0.5% charge loss

Toyota solid state battery prototype

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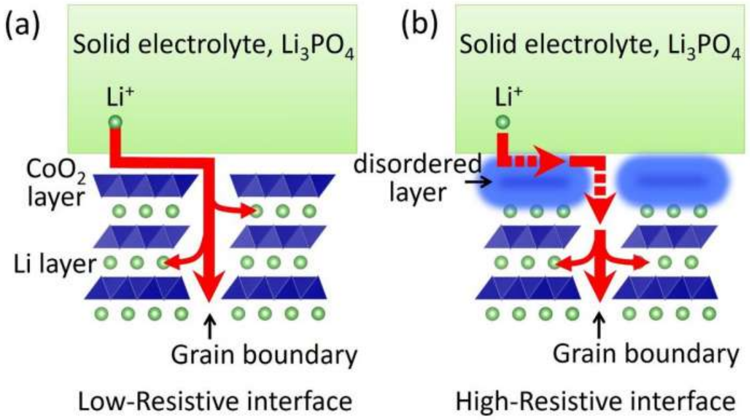
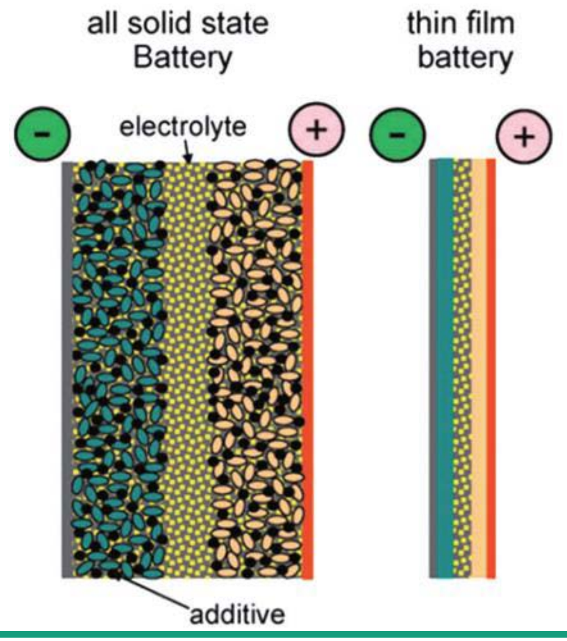
Solid state lithium batteries
Challanges

- **Current research topics**
  - Developing **better conducting** solid electrolytes
  - Designing improved electrode/electrolyte interfaces to reduce **interfacial resistance**
  - **Improving Li-ion conductivity** in active materials.

- **Current production challenges**
  - Price for production -150 $/kWh
  - Reduce thickness of separator
  - High throughput production Roll2Roll





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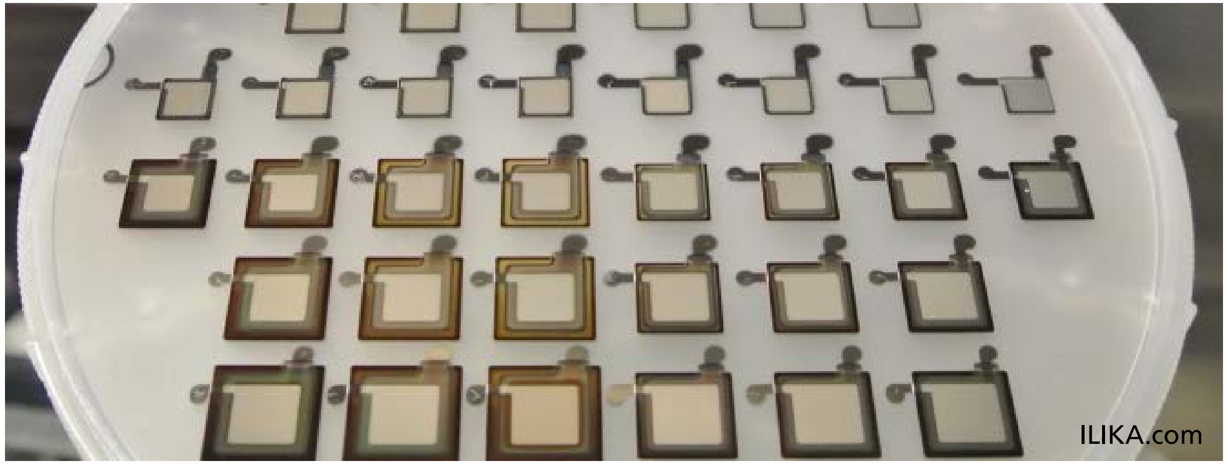
Current production of thin film batteries

- Comparable to semiconductor industry with batch-wise and discontinuous deposition technology
- Small production and pilot lines
  - Commercially available: 0.7 mAh battery: 11 US$
  - Tesla Model S (85kWh) → cost ~ 1.4 Bil US$ (1.2 Bil €)



Current production of SSLB

STMicroelectronics
EFL700A39
25.4mm x 25.4mm
200µm thickness
200mg weight

intern
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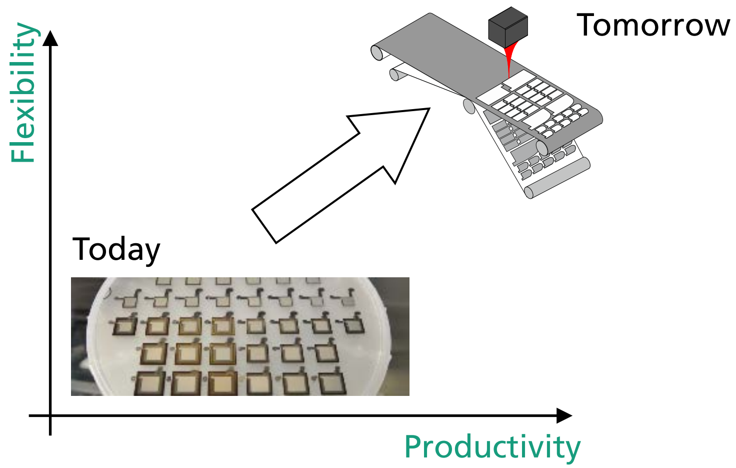
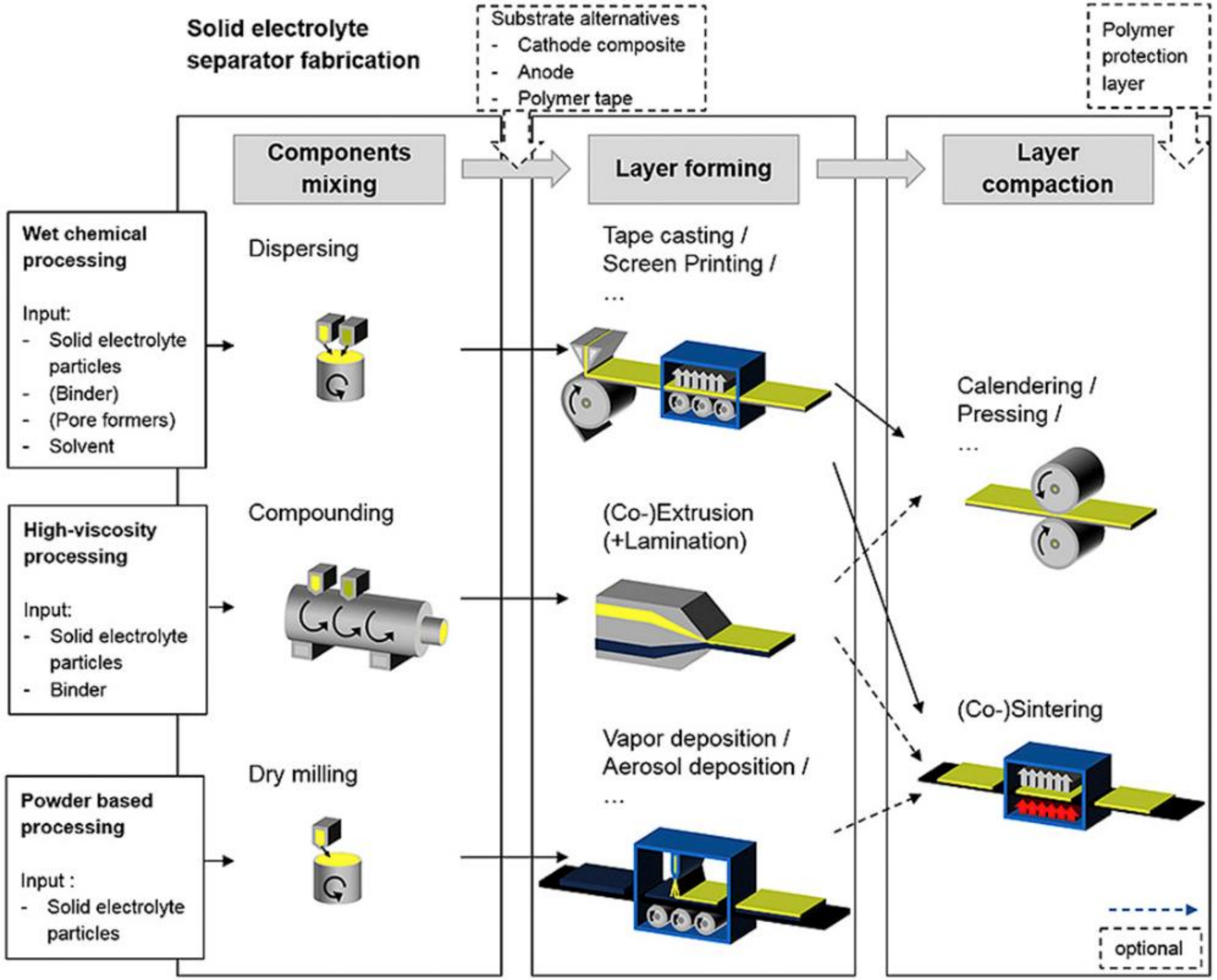
Continuous production of thin film batteries

Decollating of SSLBs – Challenge & Solution

- Changing from batch-wise process to a roll-to-roll production
- Continuous deposition with high rates possible in roll-to-roll
- New processes and equipment are necessary





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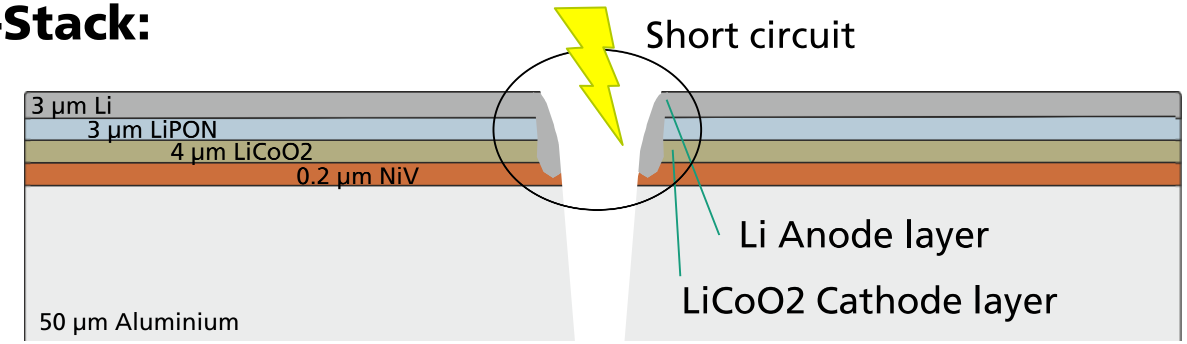
Ultra short pulse micro processing

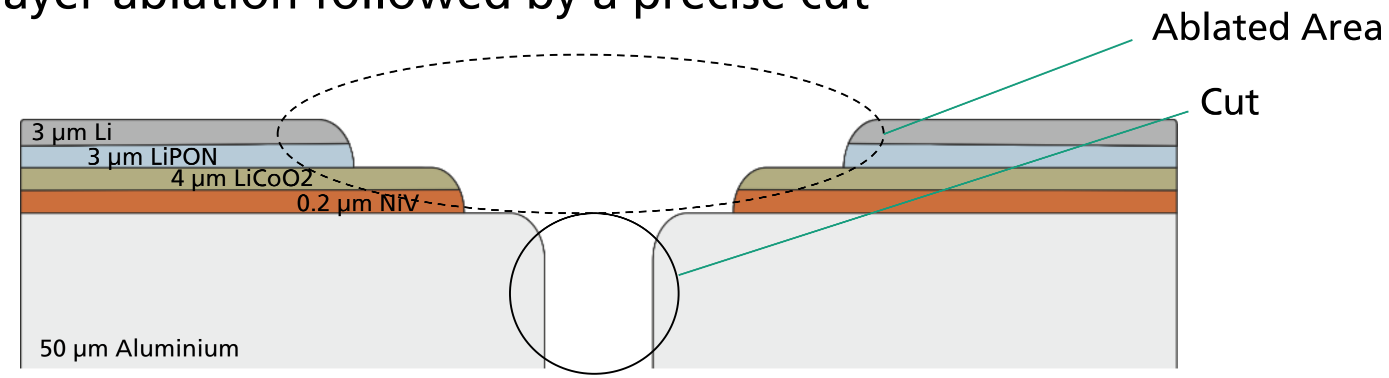
SSLB - ablation and cutting without short circuits

- Conventional cutting (cw-laser/knife) can lead to short circuits when anode and cathode layer get in contact through melt or residues

LIPON SSLB-Stack:

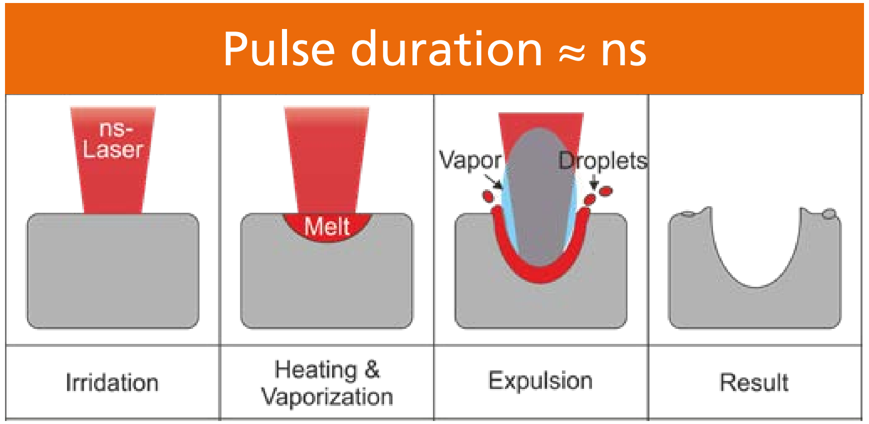


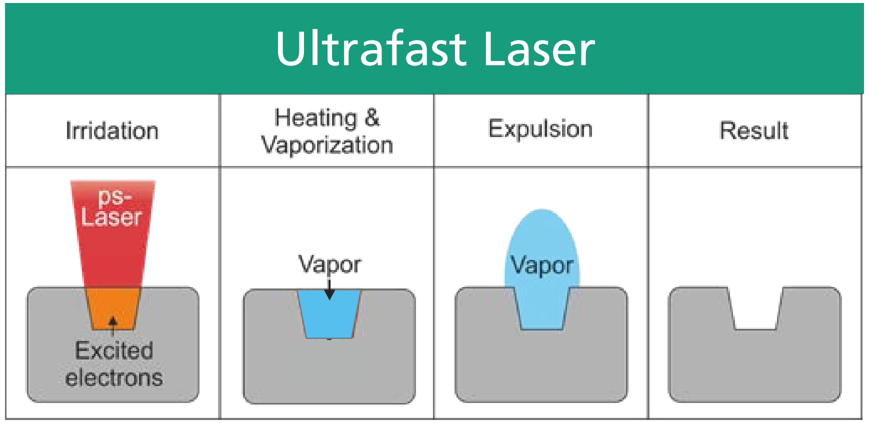
- Solution: Layer-by-layer ablation followed by a precise cut



USP laser material processing

Process basics





Time Scales for Energy Transfer

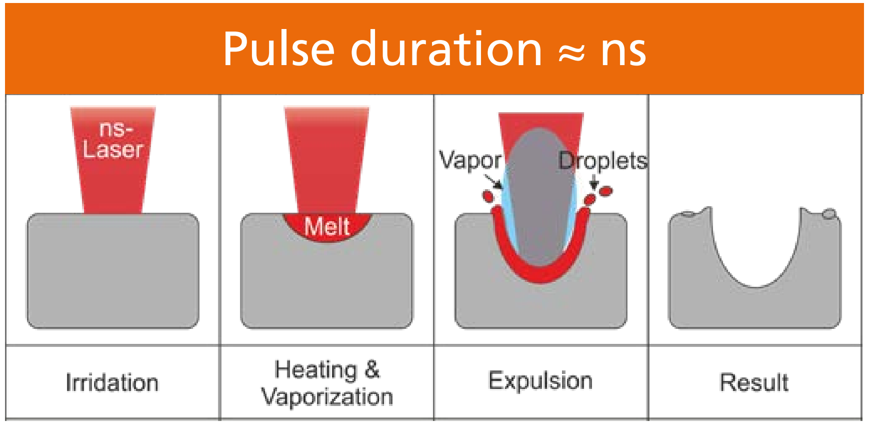
- Photon – Electron: <10 fs
- Electron – Electron: <100 fs
- Electron – Lattice: 1-10 ps

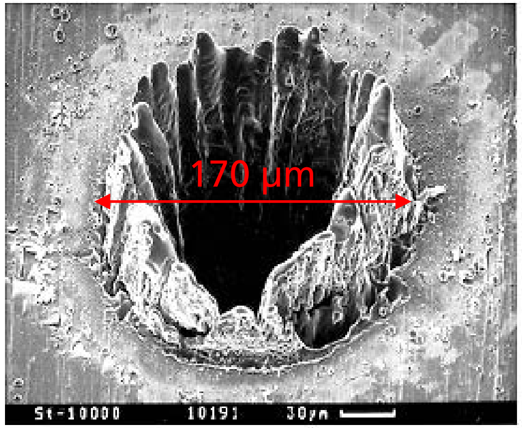
Comparison Ultrafast vs. short pulse lasers

- No interaction of radiation with vapour and melt
- Ablation mainly by vapourisation
- Minimal thermal influence

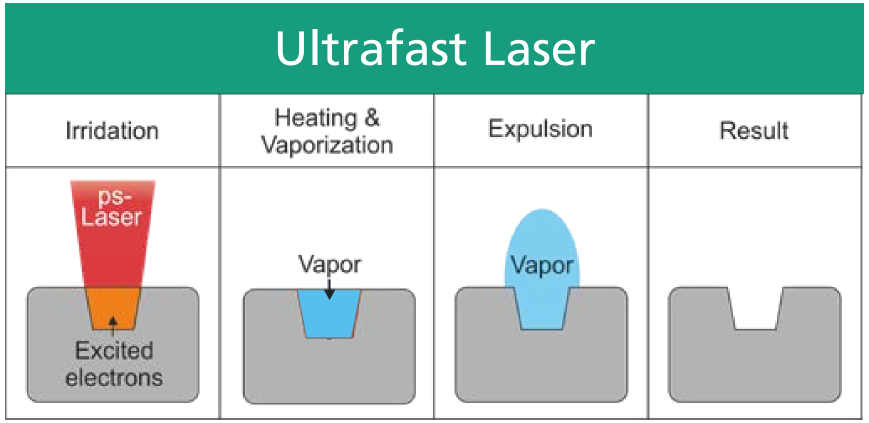
USP laser material processing

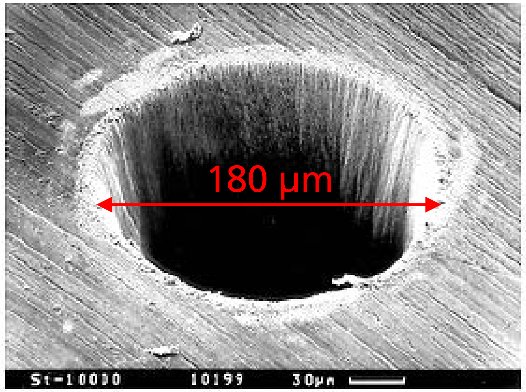
Results in material processing





10 ns

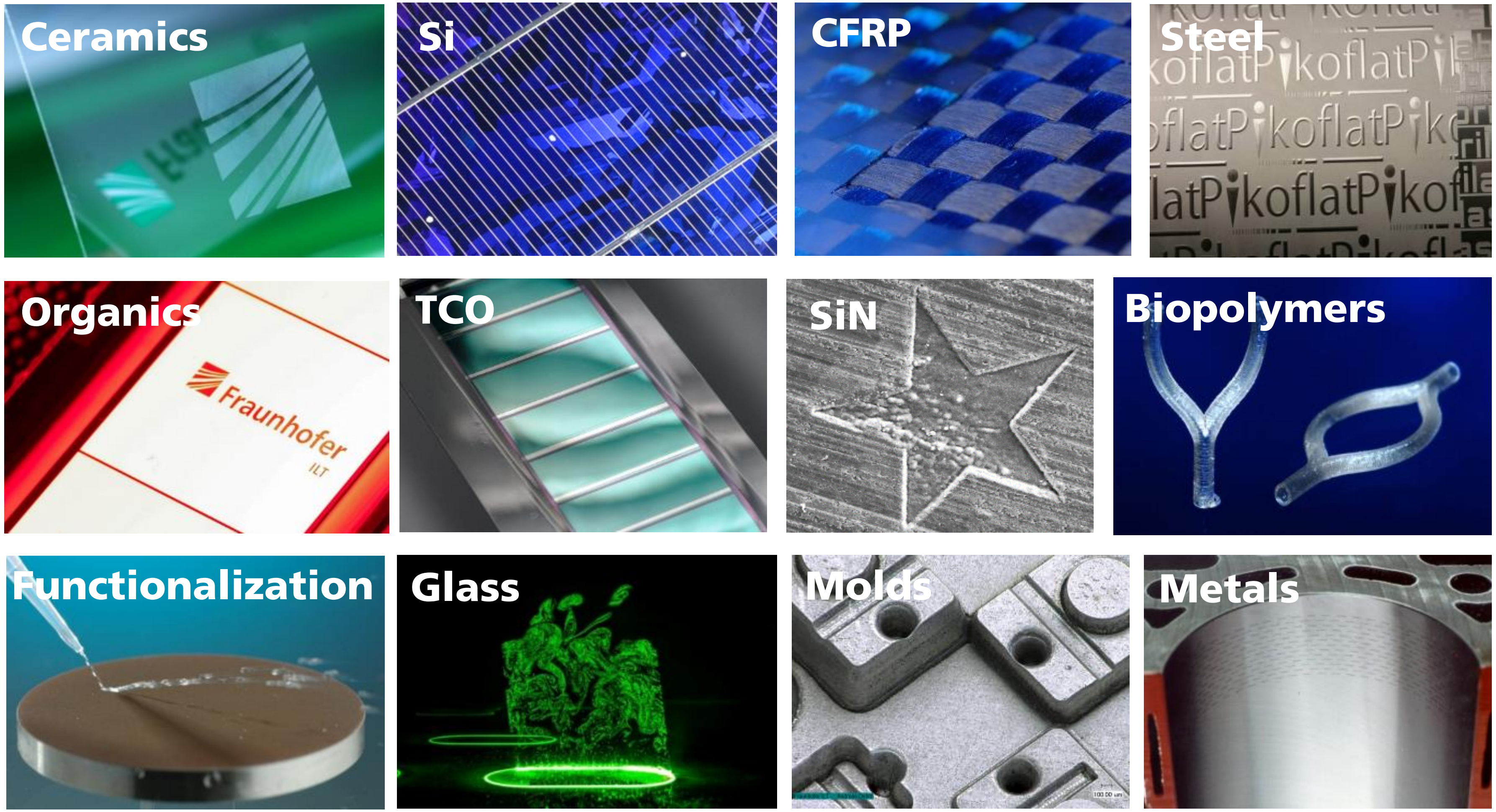




100 fs

USP laser material processing

Materials and processes



Thin film ablation

<table>
<tr><th>Flexible PV (OPV, CIGS)</th><th>Thin film PV on glass (Si, CdTe, CIGS)</th><th>OLED lighting (on glass)</th><th>Displays on glass</th><th>Organic electronics (sensors, circuits)</th><th>Thin film batteries</th></tr>
<tr><td colspan="2">P1 P2 P3 patterning</td><td>Removal of barrier layers</td><td colspan="2">Isolation scribing</td><td>Cathode surface structuring</td></tr>
<tr><td colspan="2">Edge deletion</td><td>TCO structuring</td><td colspan="2">Contact opening</td><td>Decollating</td></tr>
<tr><td>Polymer welding for encapsulation</td><td colspan="4">Glass welding for encapsulation</td><td>Drilling</td></tr>
<tr><td></td><td colspan="4">TCO annealing</td><td></td></tr>
<tr><td></td><td colspan="2">Transfer printing of metal grids</td><td></td><td></td><td></td></tr>
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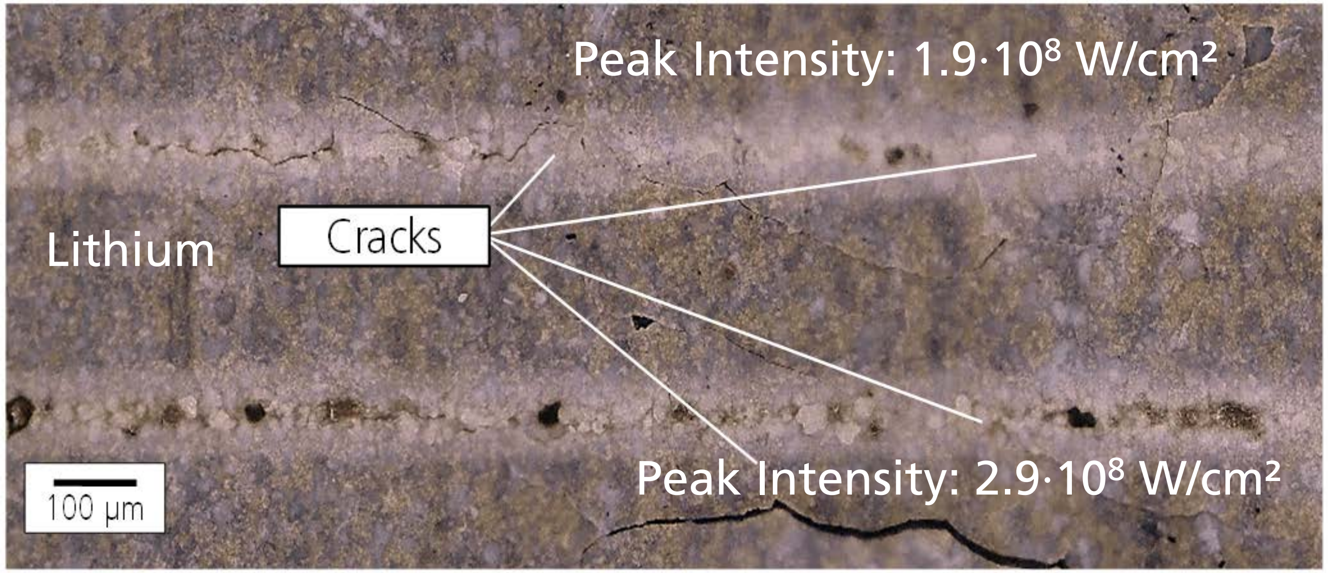
- All processes highlighted in green include some form of selective ablation

USP laser processing of SSLBs
SSLB material ablation

27ns

$2\text{-}3 \cdot 10^8$ W/cm²

Discoloration due to ablation of SSLB with nanosecond Pulses



- Irradiation the upper layers of the thin film battery with nanosecond-laser
- LiPON and Lithium absorb less than 8% of the incoming laser radiation
- Different thermal expansion behavior of LiPON and LiCoO2 layer lead to a detachment of the Lithium and LiPON layers from the underlying LiCoO2 layer

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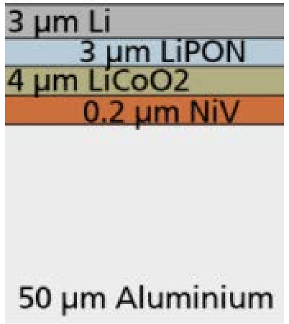
USP laser processing of SSLBs

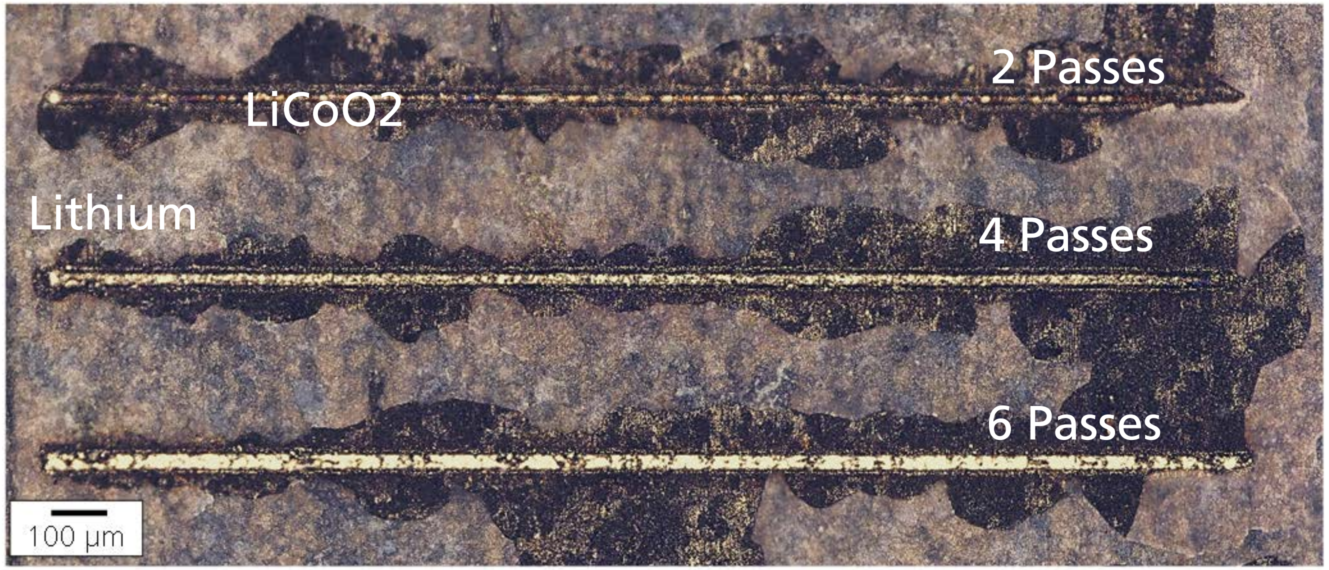
SSLB material ablation

27ns

1.9·10⁸ W/cm²

Ablation of SSLB with nanosecond Pulses and increasing repetitions





- Ablation of lithium cobalt oxide-cathode layer and subsequently the aluminum substrate by increasing repetitions
- Ablation is characterized by large outbreaks on both sides of the ablation line
- High thermal impact and low peak intensity lead to an undefined ablation of the lithium-anode layer and the LiPON-electrolyte due to photomechanical ablation

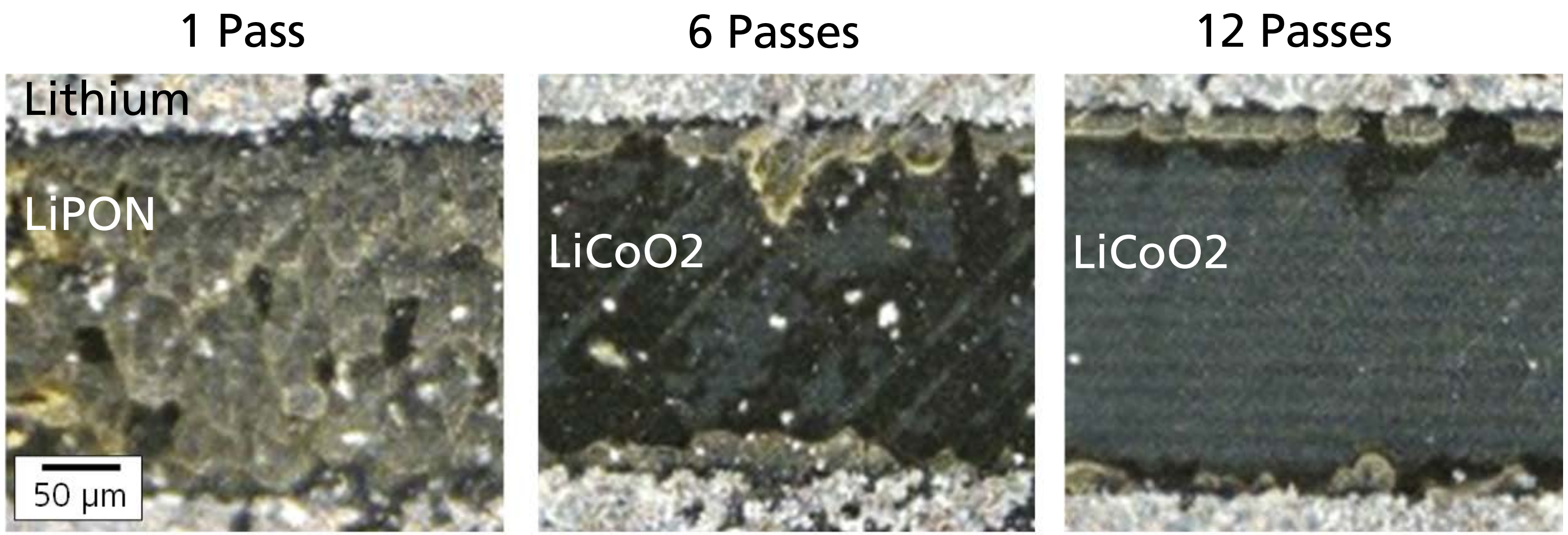
USP laser processing of SSLBs

SSLB material ablation

10ps

$1.6 \cdot 10^{11}$ W/cm²

Ablation of SSLB with picosecond pulses and increasing repetitions



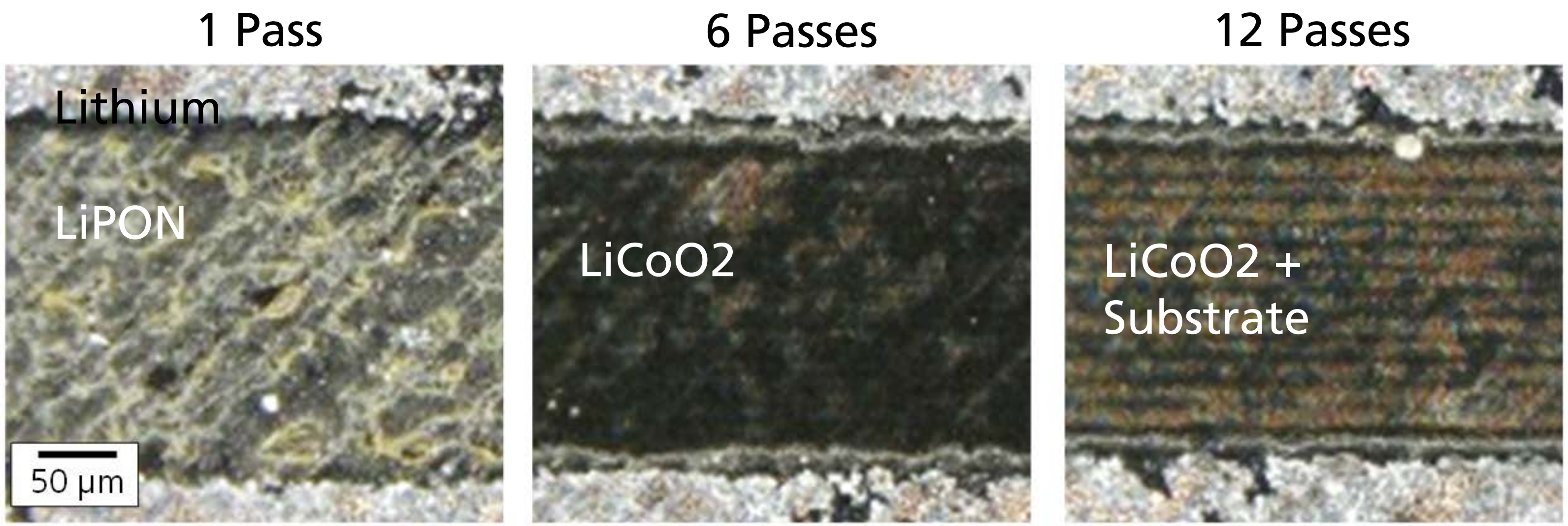
- Irradiation of the upper layers of the thin film battery with picosecond-laser
- In contrast to the ablation with nanosecond pulses, a controlled layer-wise ablation can be realized
- Increasing number of passes results in a gradual removal of the lithium cobalt oxide layer (black)

USP laser processing of SSLBs

SSLB material ablation

200fs
$7.3 \cdot 10^{12}$ W/cm²

Ablation of SSLB with femtosecond pulses and increasing repetitions



- Irradiation of the upper layers of the thin film battery with femtosecond-laser
- LiPON-electrolyte surface is characterized by a multitude of small cracks
- Lower heat generation in the $LiCoO_2$-layer compared with picosecond ablation
- Photomechanical ablation mechanism is less predominant than in the case of picosecond irradiation

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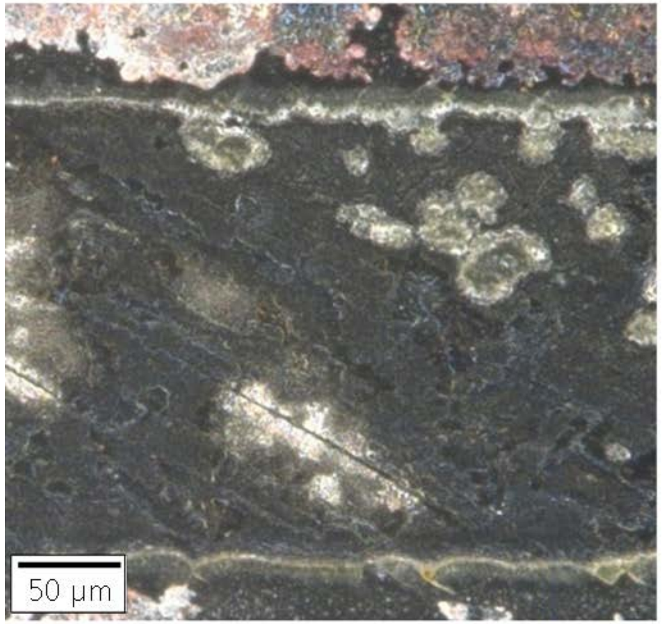
USP laser processing of SSLBs
SSLB material ablation

Comparison of Ablation of SSLB with Picosecond and Femtosecond pulses (10 Passes)

- **Contour-accurate ablation** can be achieved by using femtosecond pulses as opposed to the ablation with pico/femto second pulses which is characterized by small outbreaks near the rim
- The use of nanosecond pulses results in **blast-off ablation** leading to very broad areas with uncontrolled blasting of the layers

200fs – 10 passes



10ps – 10 passes

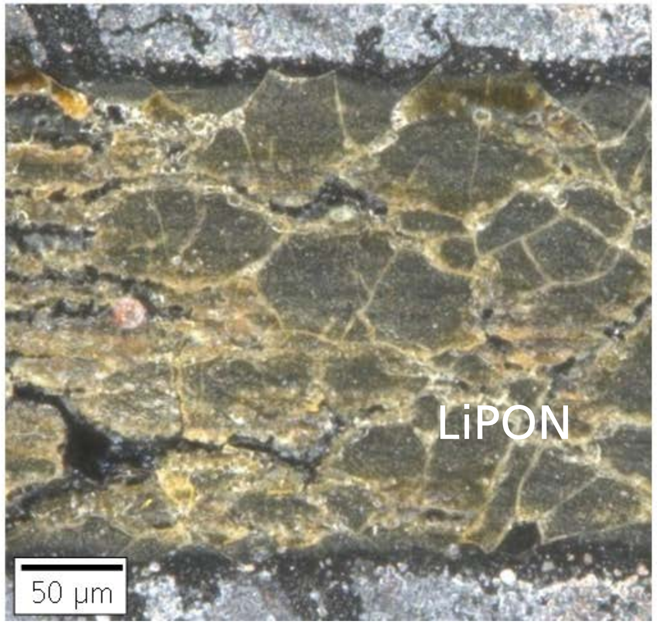
USP laser processing of SSLBs

SSLB material ablation

Comparison of Ablation of SSLB with Picosecond and Femtosecond pulses (1 pass)

- Glass-like **LiPON cannot be removed** in a controlled manner with pulses > 10 ps
  - LiPON-surface irradiated with 10 ps pulses consists of many large fragments with no change in structure and texture
- LiPON-surface irradiated with 200 fs pulses shows discoloration and micro-cracks

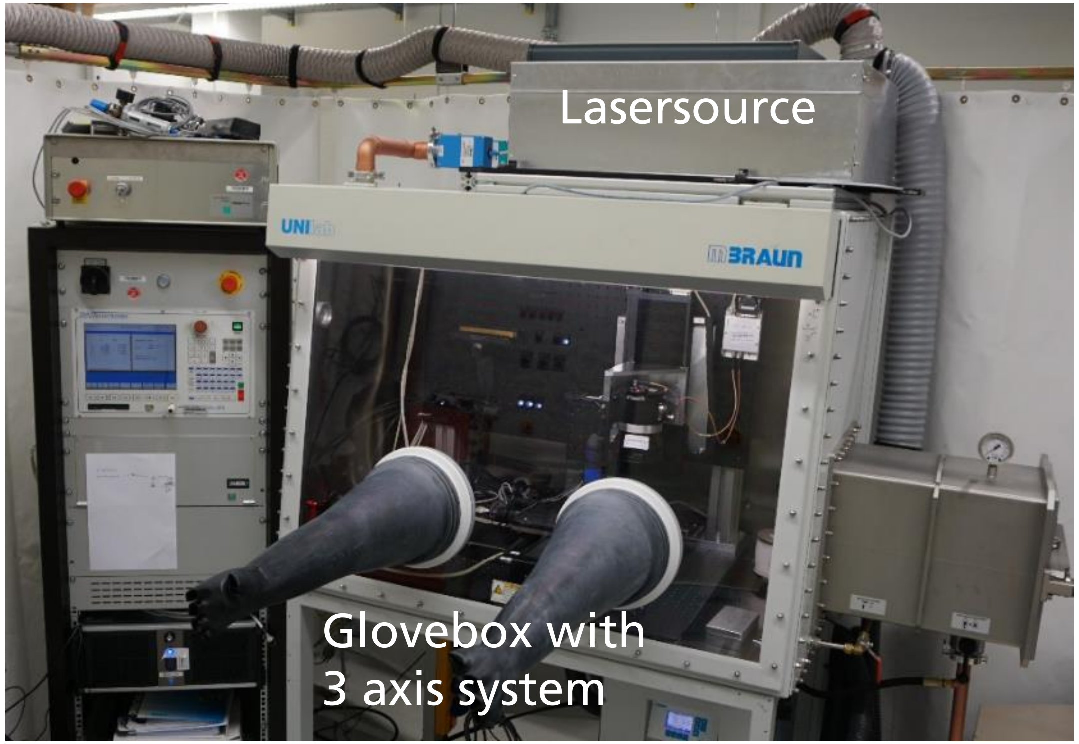
200fs – 1 pass



10ps – 1 pass

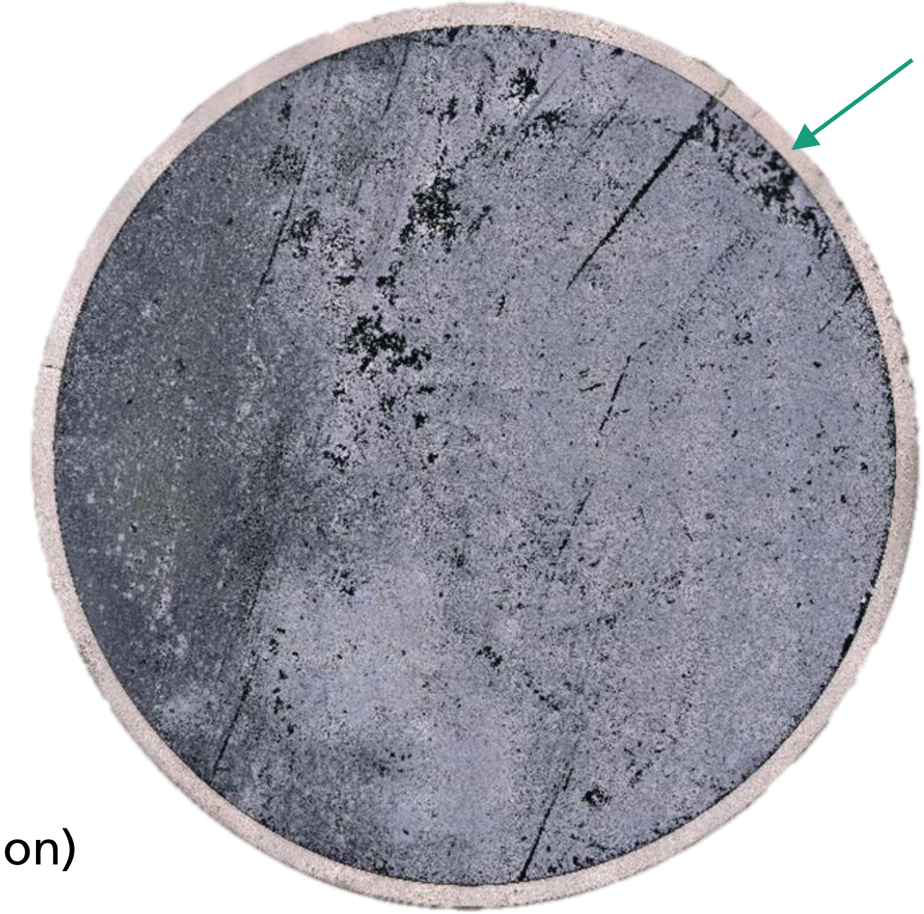
Processing results

SSLB - ablation and cutting without short circuits



- Laser ablation in inert atmosphere (0.5ppm Argon)
- Geometrically flexible cutting

Ablated area



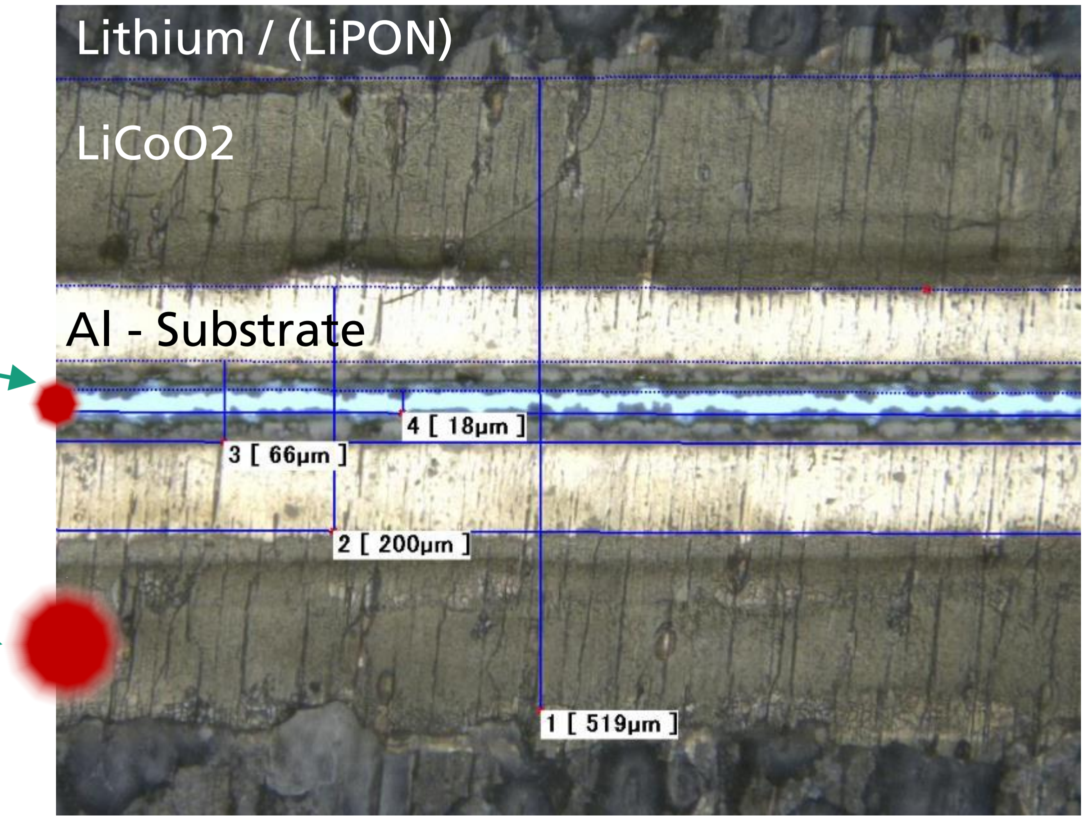
- Battery with diameter 20 mm
  (Exposed to air for imaging)

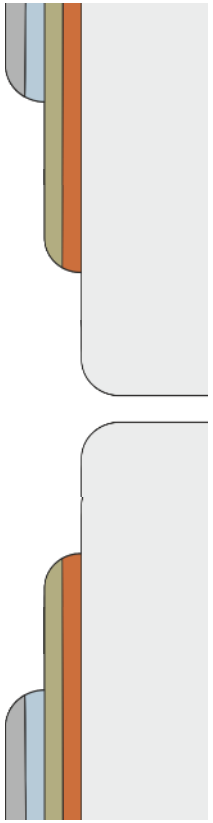
Processing results
SSLB - ablation and cutting without short circuits

Process variation for cutting of full stack

Narrow Focused beam for cutting

Areal ablation with broader beam

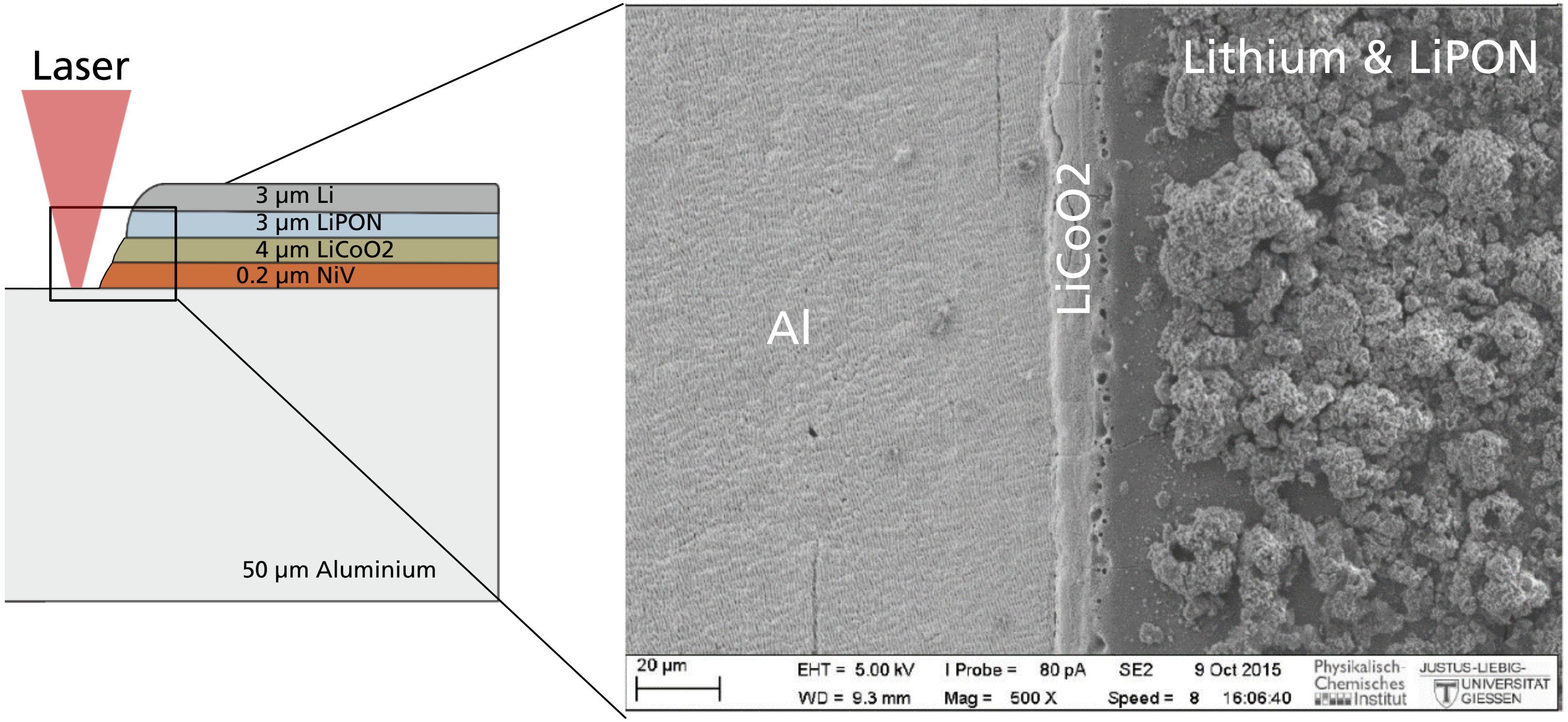




Processing results

SSLB - ablation and cutting without short circuits

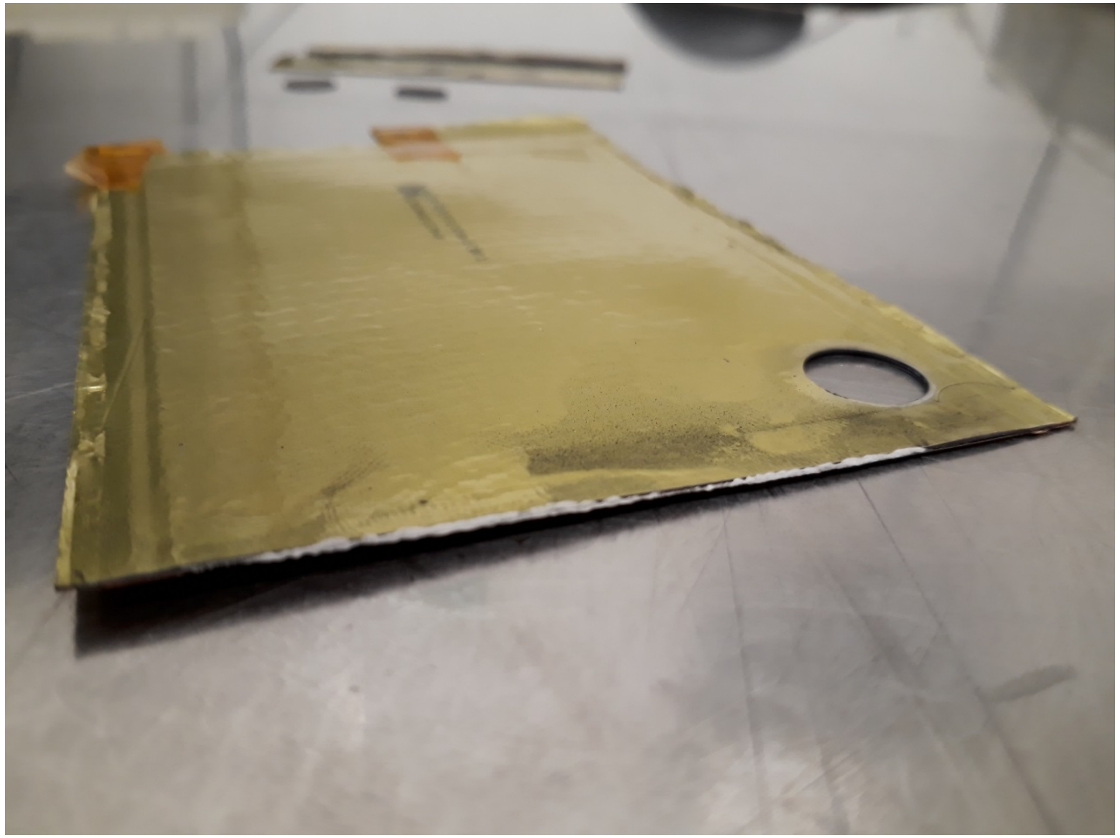
Rim of the battery



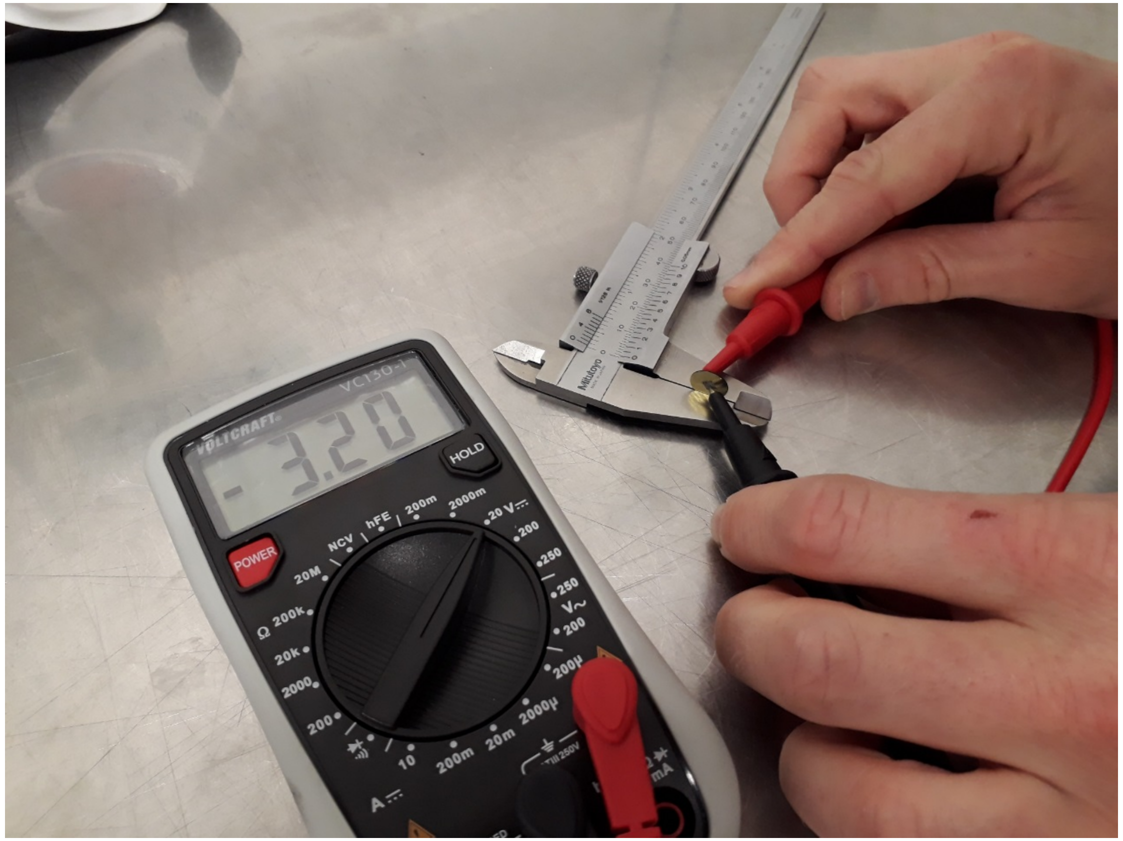
REM-Image

Processing results

SSLB - ablation and cutting without short circuits



Processed full battery stack

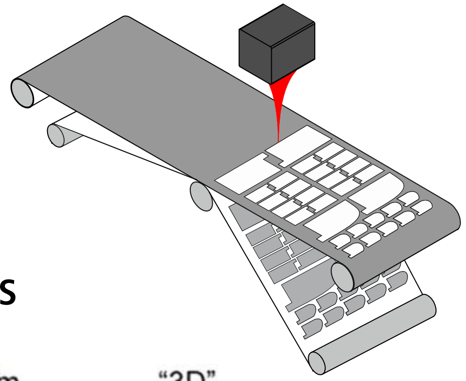


Function test of decollated battery

Outlook

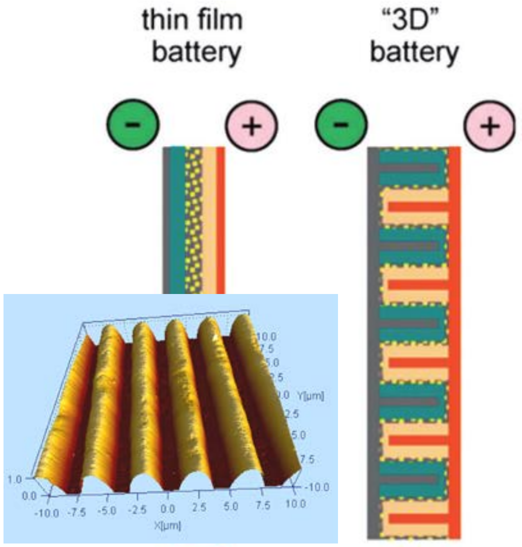
Future processing of SSLBs

- **Integration in Roll2roll production**
  →High throughput production

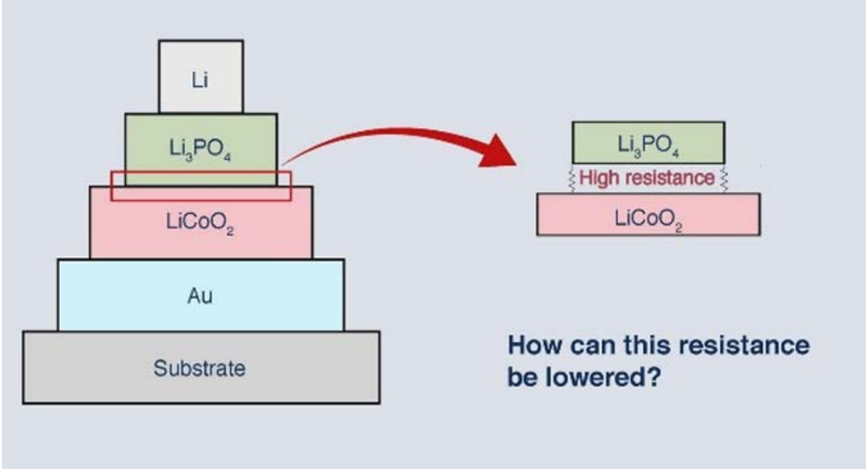


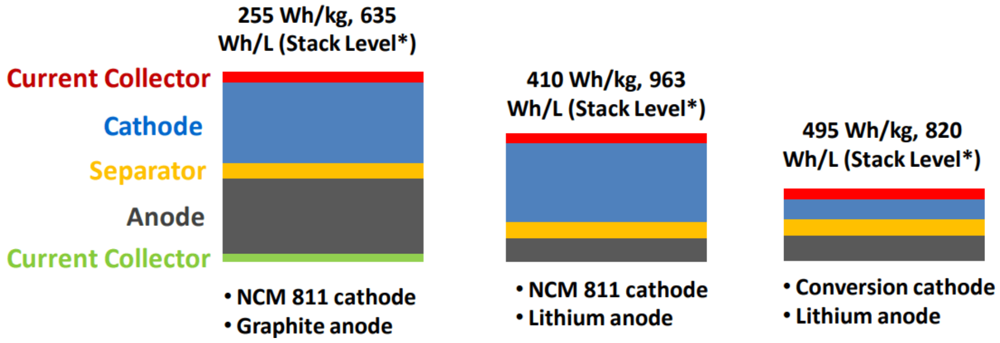
- **Fabrication/processing of thinner layers**
  → higher density

- **Surface structuring**
  → "3D battery"



- **Surface modification**
  → decreased resistance





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Many thanks for your kind attention!

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