Laser structuring and annealing of thin film electrodes for lithium-ion batteries

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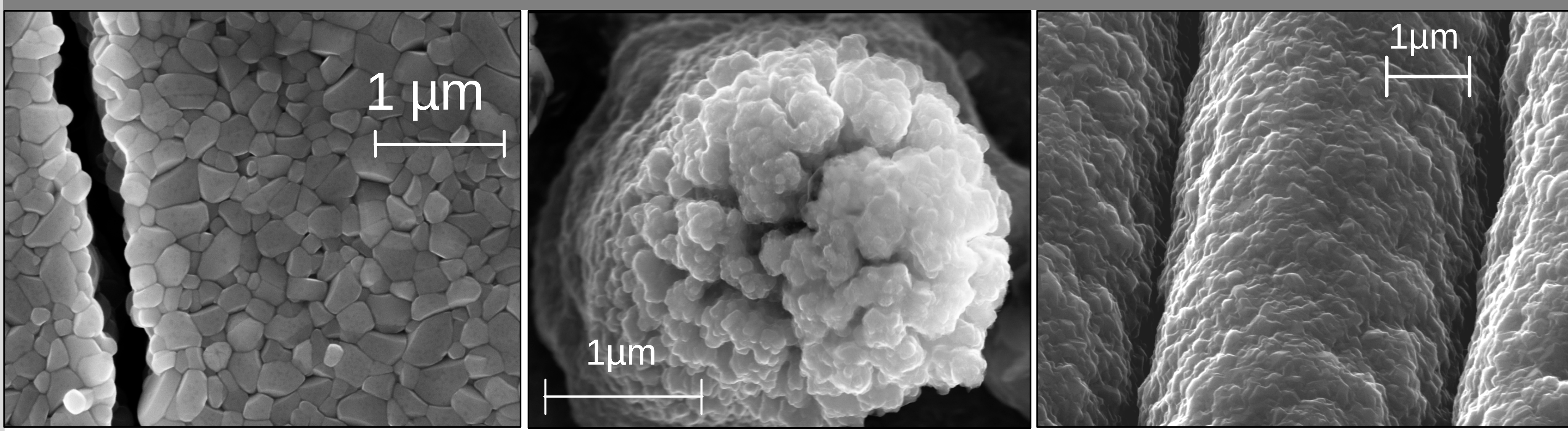


27.10.2010, 3rd International Symposium on Laser-Micromachining, Chemnitz

outline

- motivation and technical approach
- advanced materials for lithium-ion batteries
- laser structuring of thin films
- $LiCoO_2$ and Li-Mn-O as cathode materials
- SnO_2 as anode material
- summary and outlook

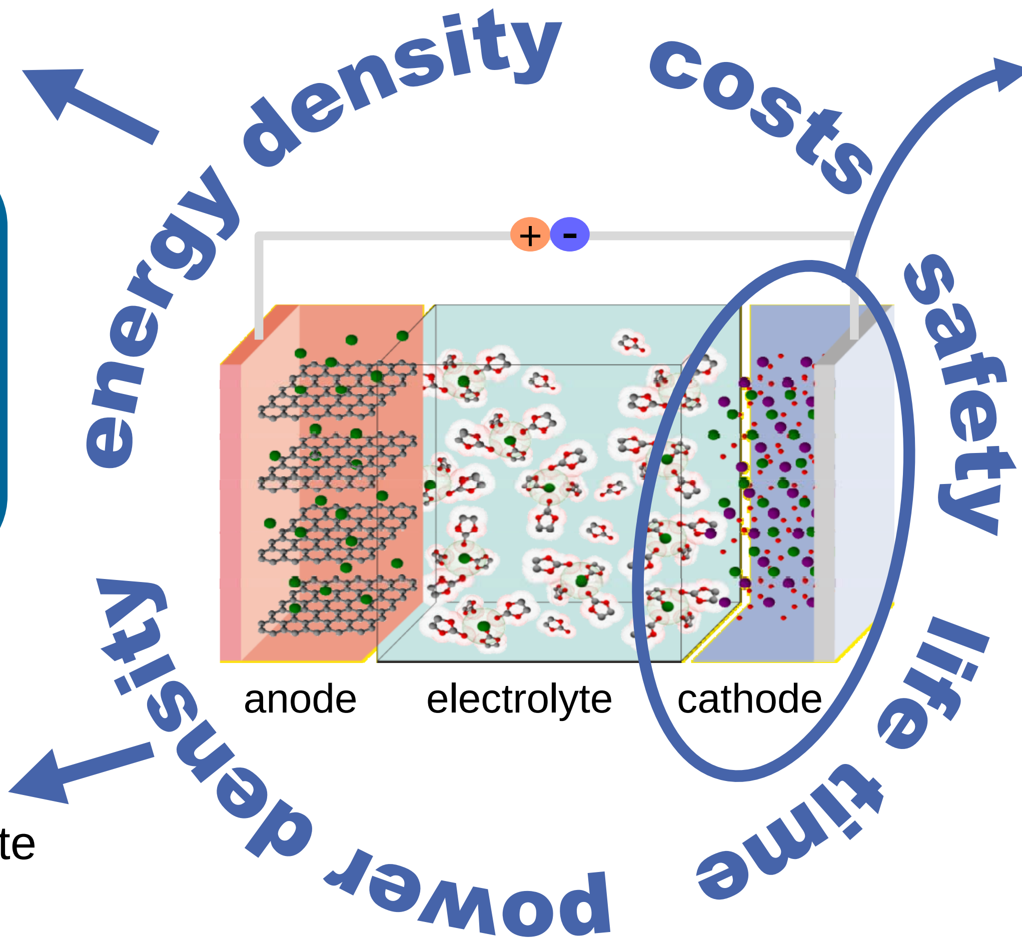
motivation

stationary power systems

energy density

- ability to store energy
- material dependent

HEV, EV



power density

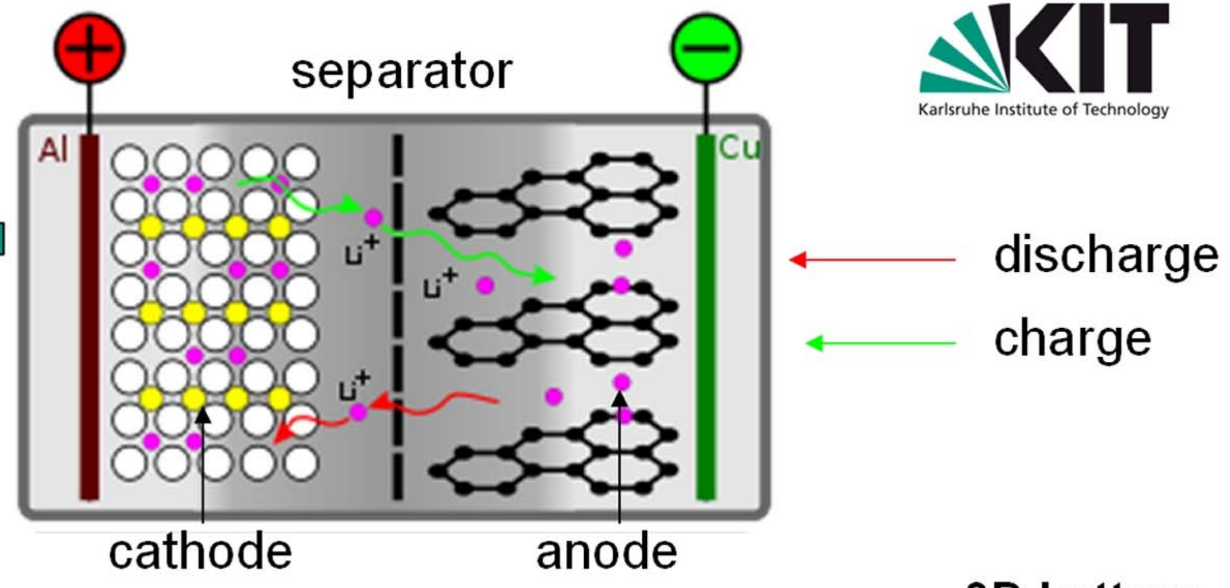
- quick power supply
- high Li^+-diffusion rate
  → enhancement of active surface

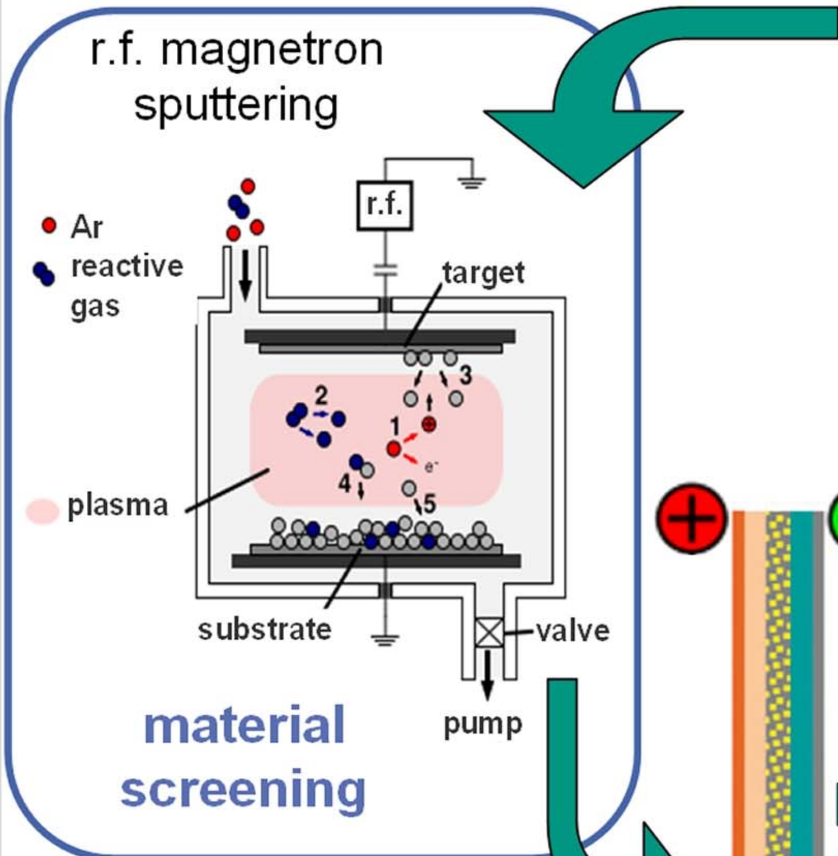
cathode

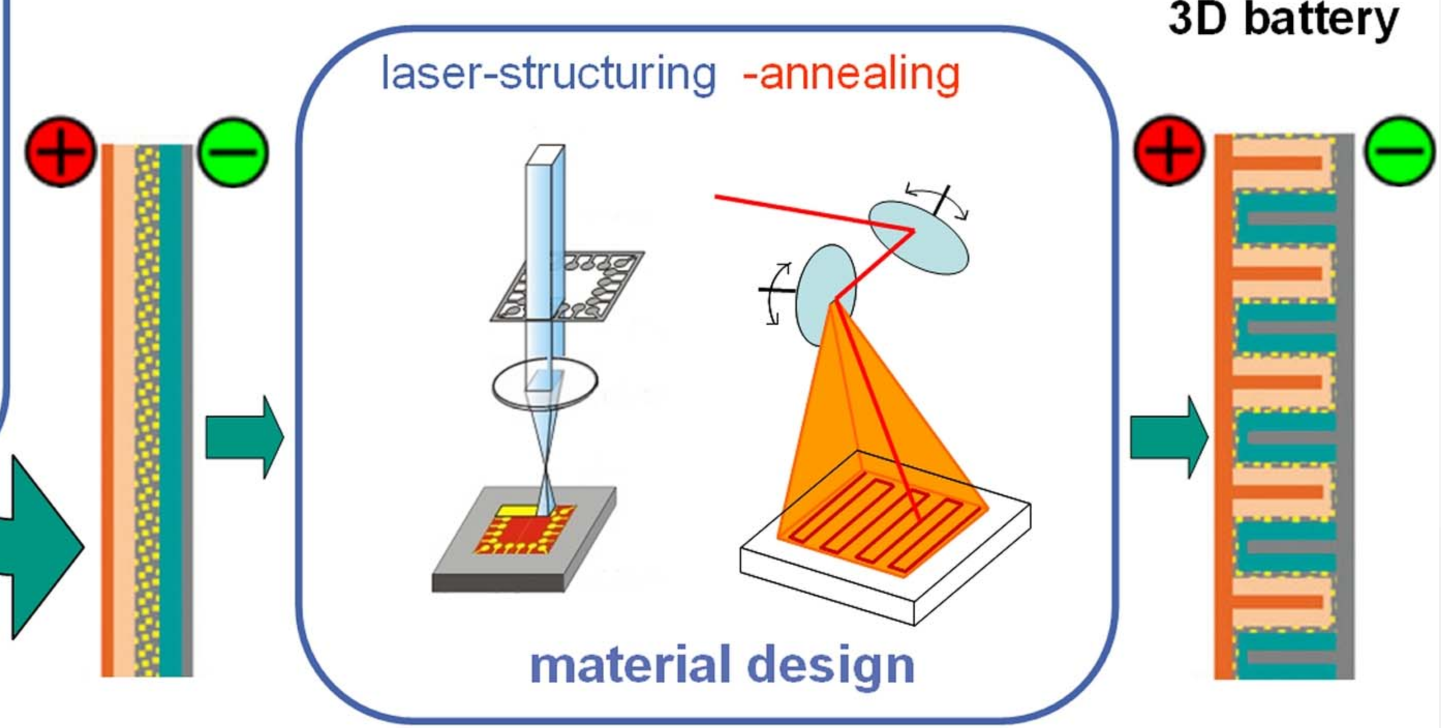
- less capacity than anode materials (graphite 378 Ah/kg)
- $LiCoO_2$ (140 Ah/kg)
- Li-Mn-O system (150-280 Ah/kg)

safety

technical approach for advanced electrode materials







advanced materials for lithium-ion batteries

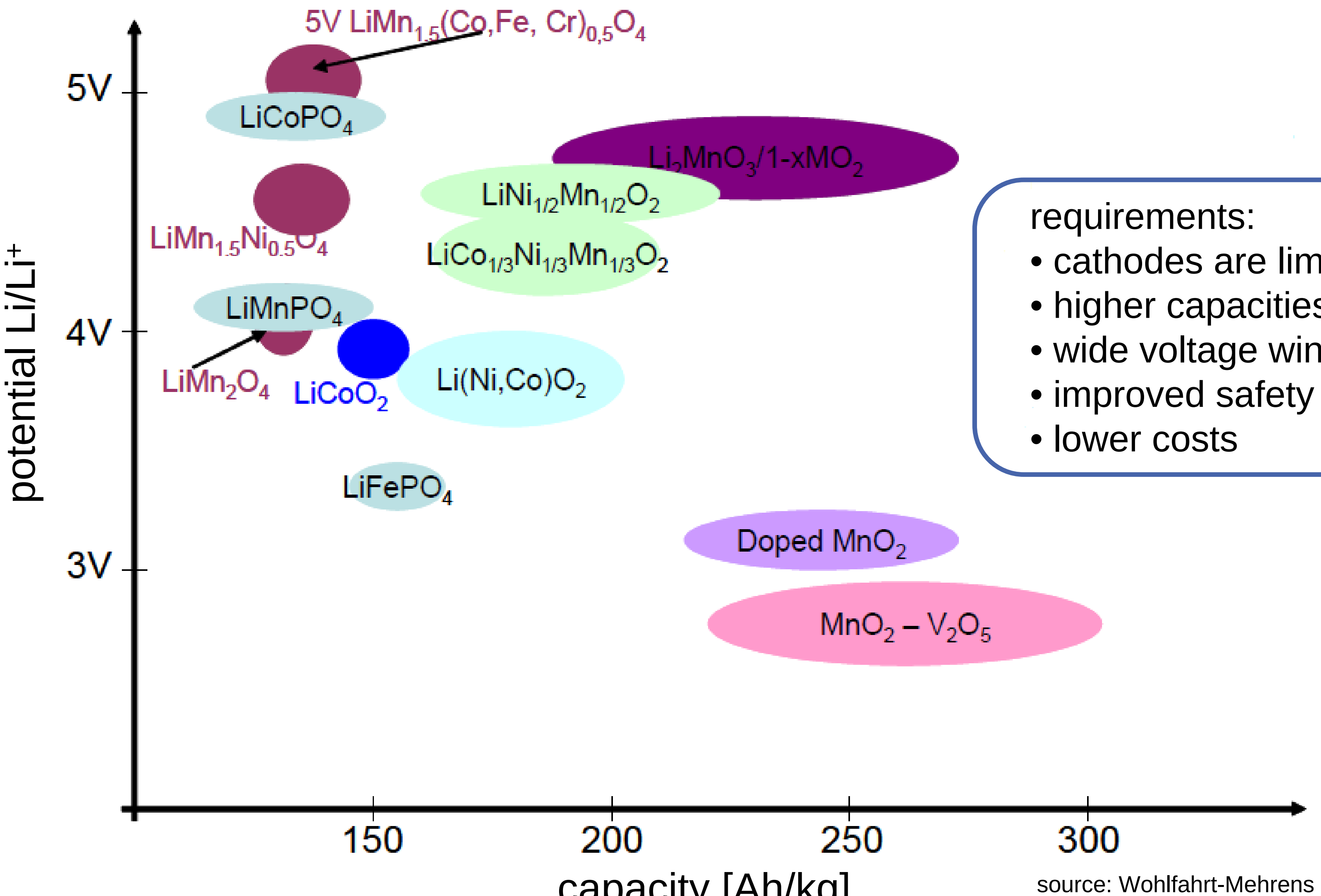
Karlsruhe Institute of Technology

cathode	*electrolyte*	*anode*
lithium manganese oxides (intercalation compounds) • cheaper • less toxicity • availability of resources • higher capacities (148-280 Ah/kg) …than $LiCoO_2$ (140 Ah/kg)	**LVSO (solid state electrolyte)** • for high thermal stability • less decomposition in the high voltage region • higher safety issues … than standard electrolyte	**SnO_2 (conversion material)** higher specific capacities (reversible 790 Ah/kg) …than graphite (378 Ah/kg)

future work:

combination of **Li-Mn-O** and **Li-Ni-O** intercalation compounds
→ increased specific capacity
→ improved stability in the high voltage region
→ structure stability

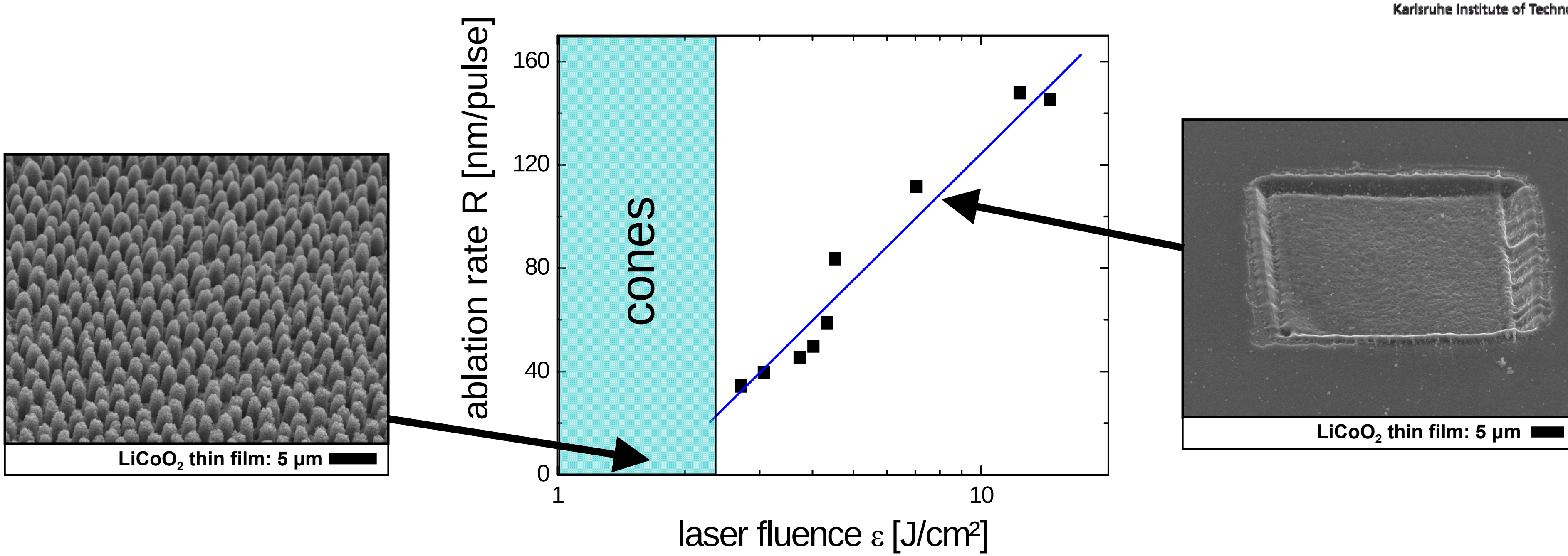
why to focus on quasi-binary systems like Li-Ni-Mn-O ?



source: Wohlfahrt-Mehrens

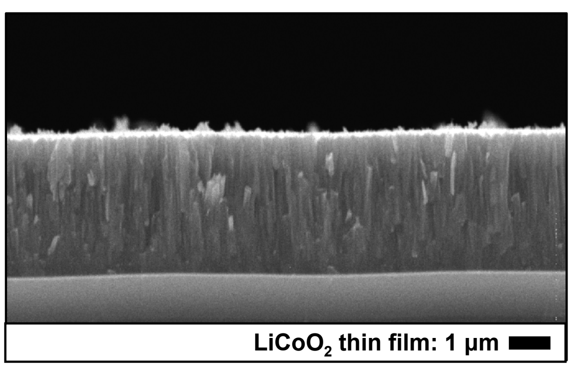
requirements:
- cathodes are limiting factor
- higher capacities
- wide voltage window
- improved safety
- lower costs

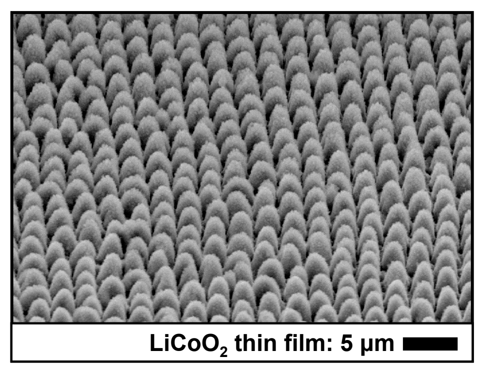
laser structuring of electrode thin films

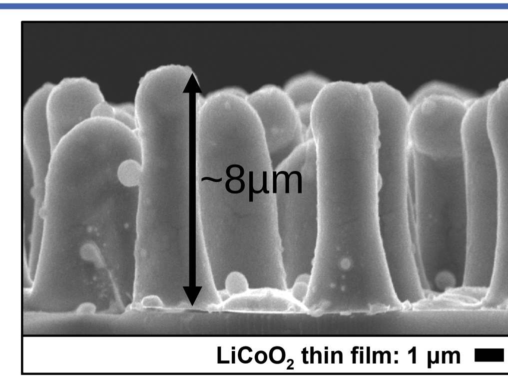


as-deposited -cross-section-	*structured -top view-*	*structured -cross-section-*

LCO

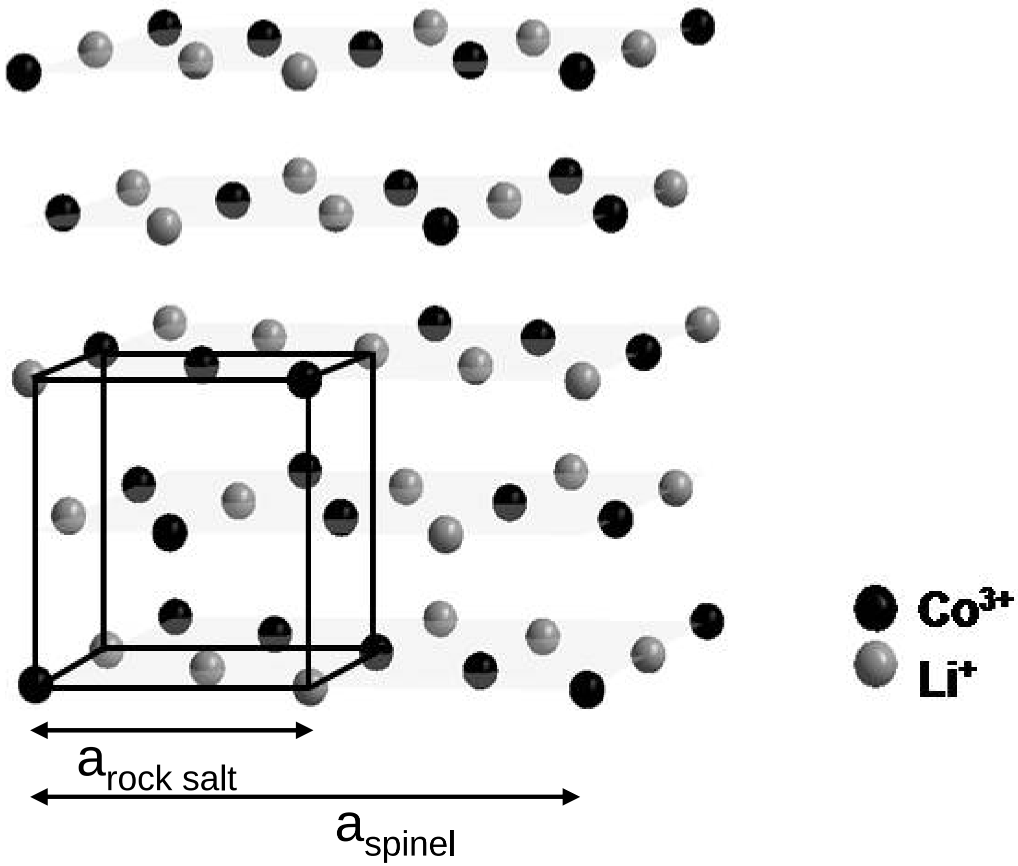






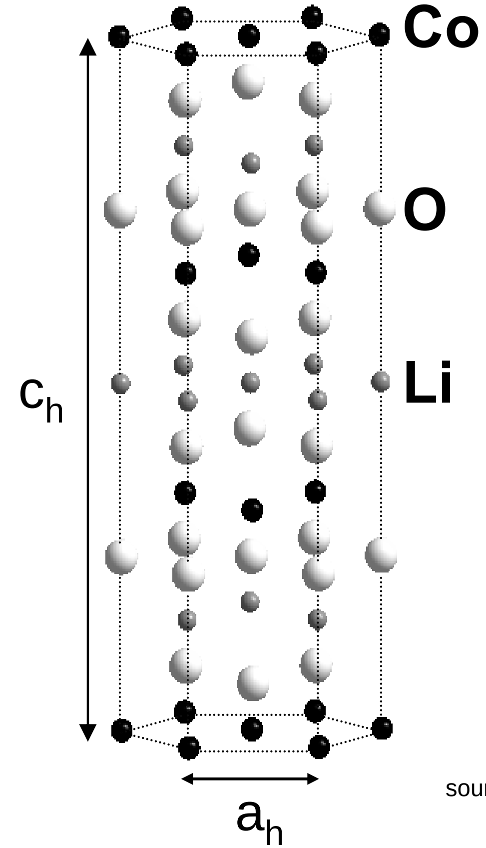
crystal structures of $LiCoO_2$ (cathode)

low temperature phase (cubic)



energy density: 80 mAh/g

high temperature phase (hex.)



formed at T ≥ 600°C

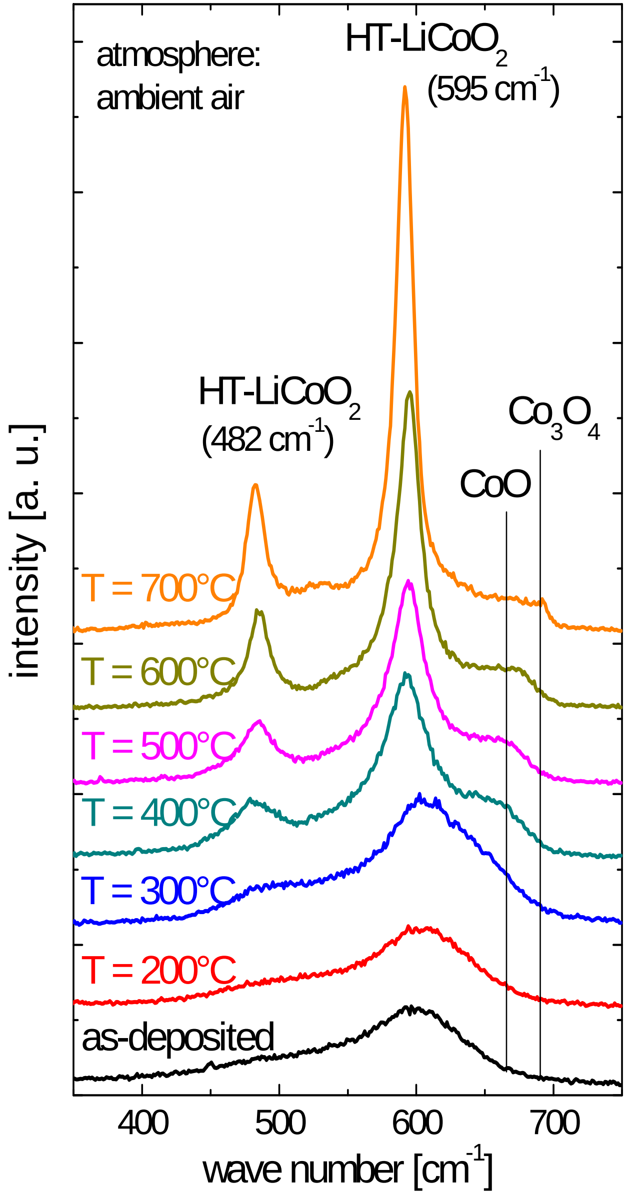
source: Kang, S.G., et al.

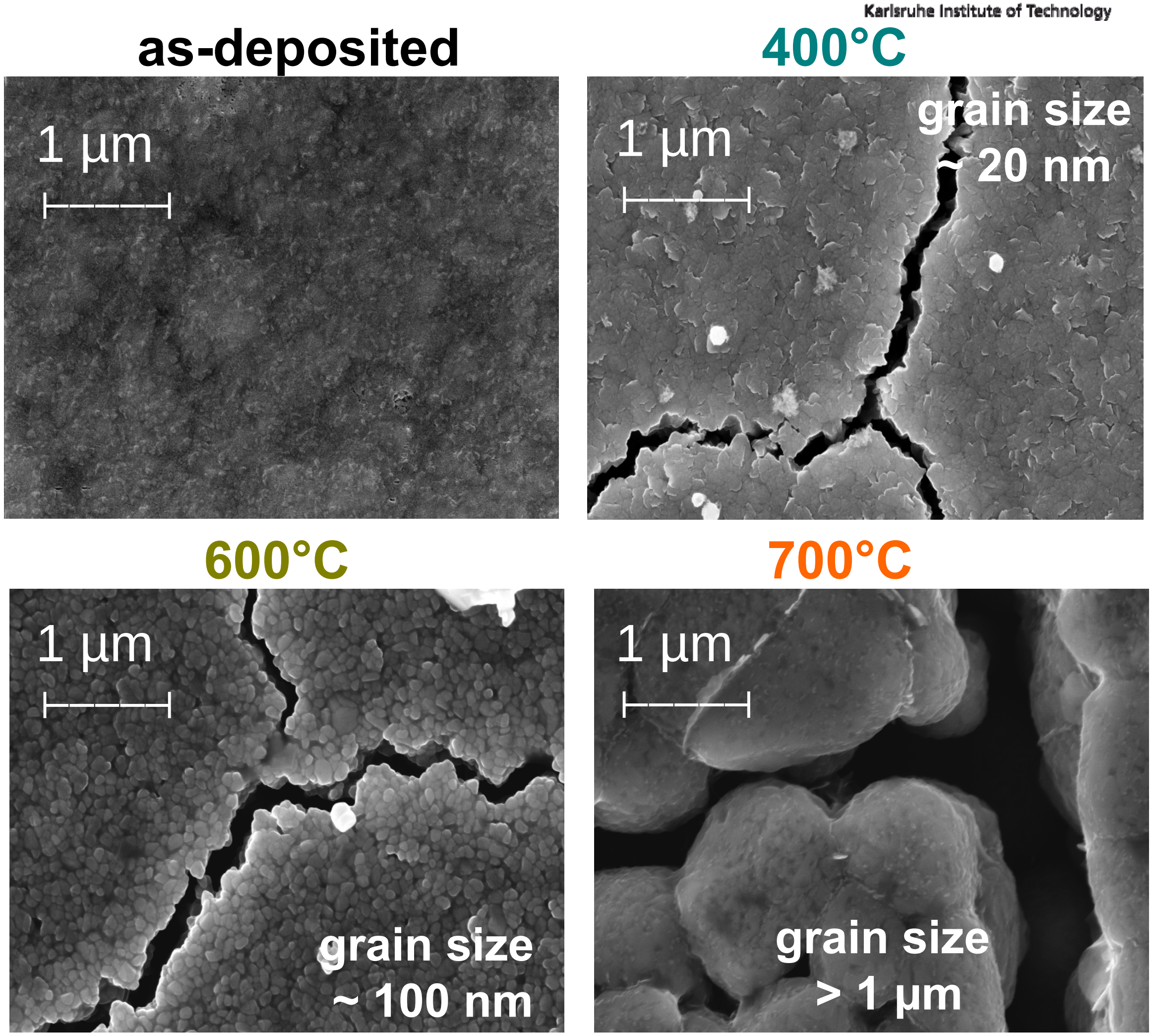
energy density: 140 mAh/g

→ differences of both phases in cation ordering within the same oxygen sub-lattice

laser annealing of $LiCoO_2$ thin films

micro-Raman spectroscopy (surface information)



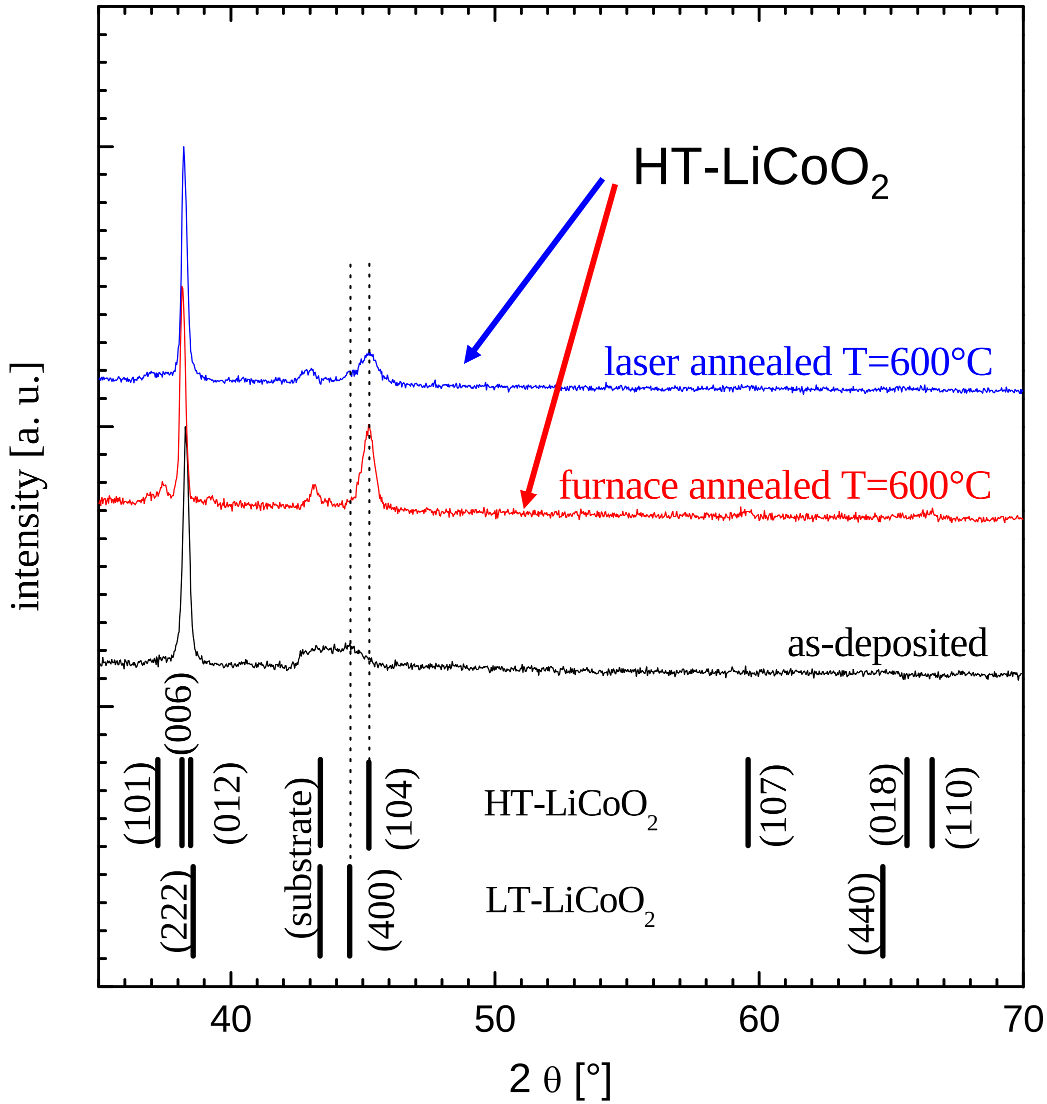


→ crack formation due to laser annealing

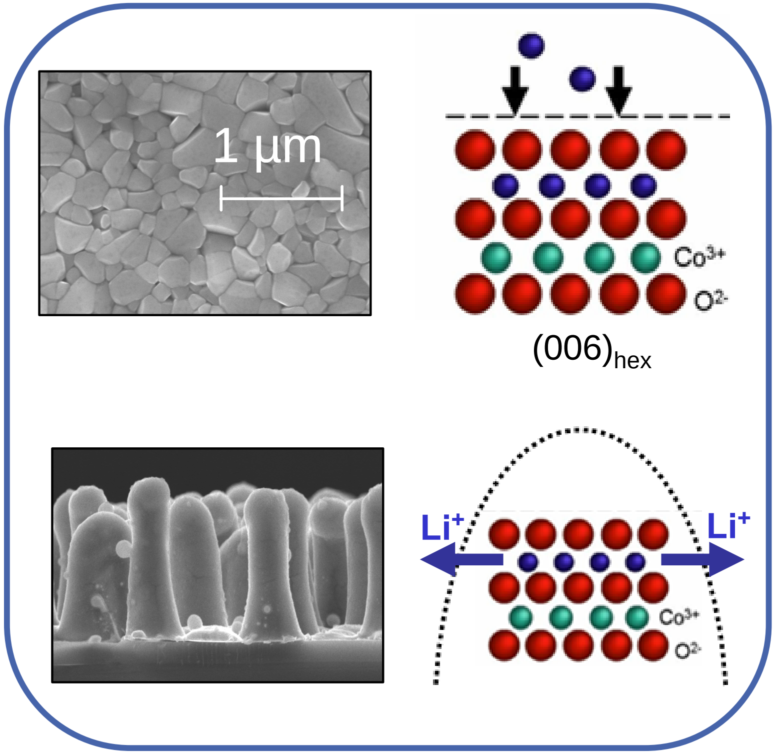
→ enhanced grain growth at T>600°C

influence of laser structuring and annealing time on crystallinity, topography and lattice orientation of $LiCoO_2$

X-ray diffraction (bulk information)



crystalline texture, topography and lattice orientation

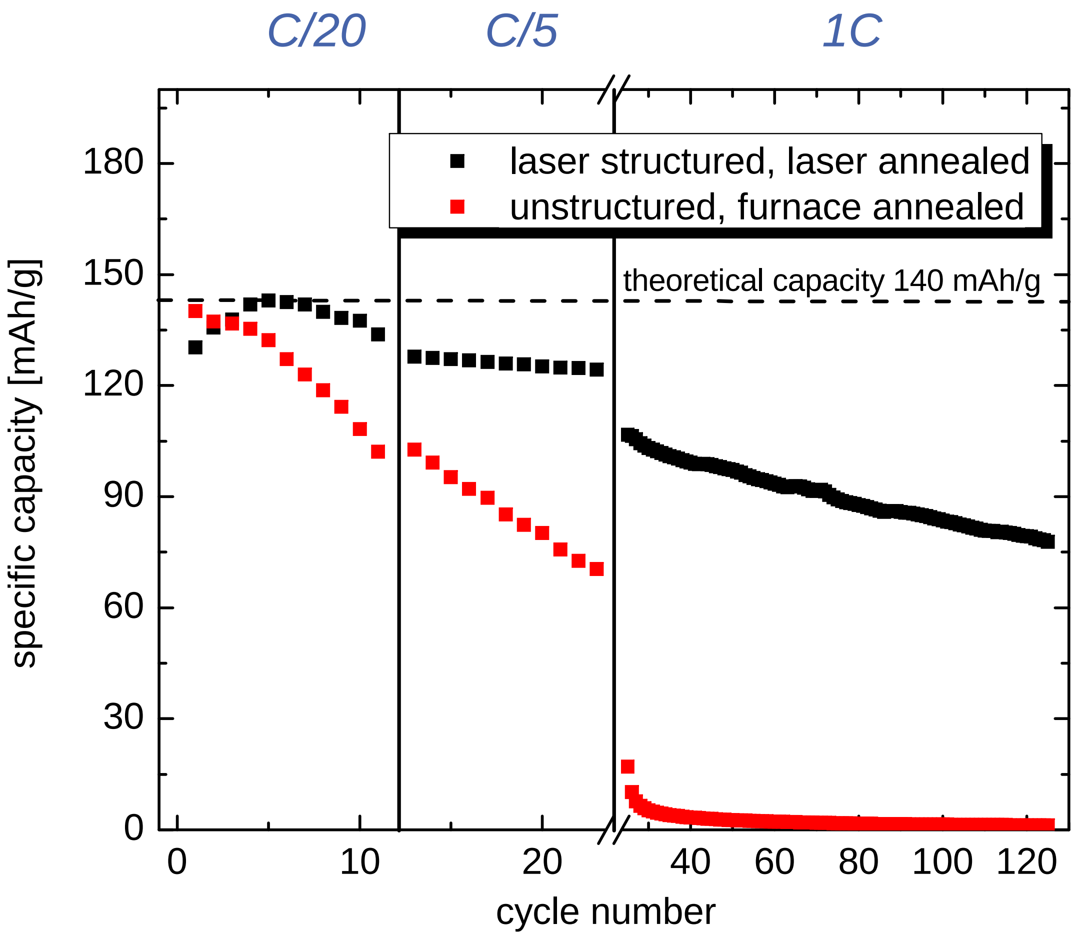


→ HT-$LiCoO_2$ $(006)_{hex}$ obtained via annealing

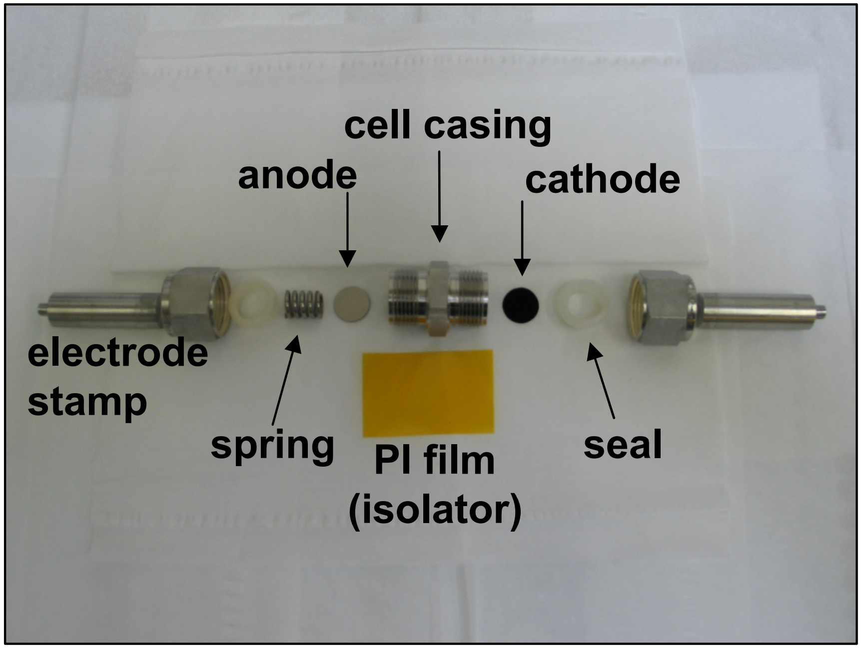
→ thermally induced lattice orientation favorably for Li^+ diffusion in structured $LiCoO_2$ thin film

battery performance of unstructured and structured $LiCoO_2$ thin films under different current rates

charge/discharge rates:



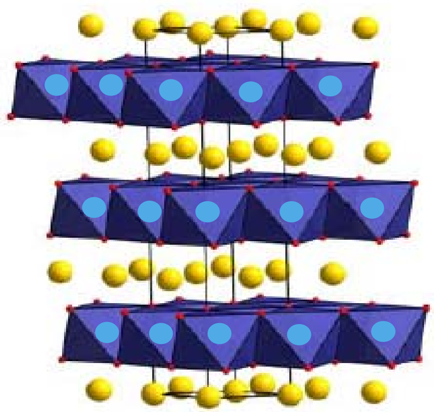
"Swagelok" test cell

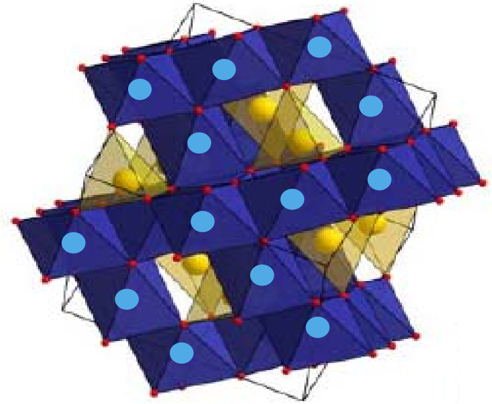


→ advanced capacity retention and cycle stability via laser structuring

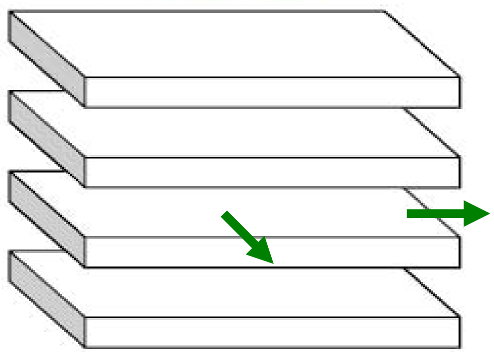
→ increase of power density especially at high charging/discharging currents

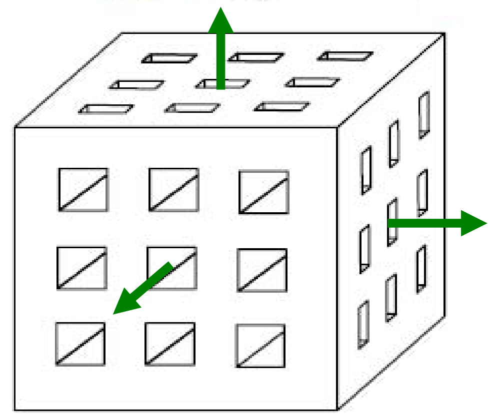
crystal structures of lithium manganese oxides (cathode)





source: Wohlfahrt-Mehrens





layered structure

- Li*M*O_2 (*M* = Ni, Co, Mn)
- $LiCo_{0,33}Ni_{0,33}Mn_{0,33}O_2$

→ 2D host structure for Li^+ diffusion

spinel structure

- $LiMn_2O_4$ (cubic)
- $Li_2Mn_2O_4$ (tetragonal)

→ 3D host structure for Li^+ diffusion

o-$LiMnO_2$ (layered)

- 285 $mAhg^{-1}$ (theoretical)
- ~150 $mAhg^{-1}$ (practical)
- changes into spinel structure (Li^+ extraction >50%, U=3 to 4V)

$LiMn_2O_4$ (spinel)

- 148 $mAhg^{-1}$ (theoretical)
- ~60-120 $mAhg^{-1}$ (practical)
- 0<x<1, cubic structure
- 1<x<2, tetragonal structure (Jahn - Teller distortion)
- Mn^{3+} occupation reaches critical 50%
- lowering of global symmetry

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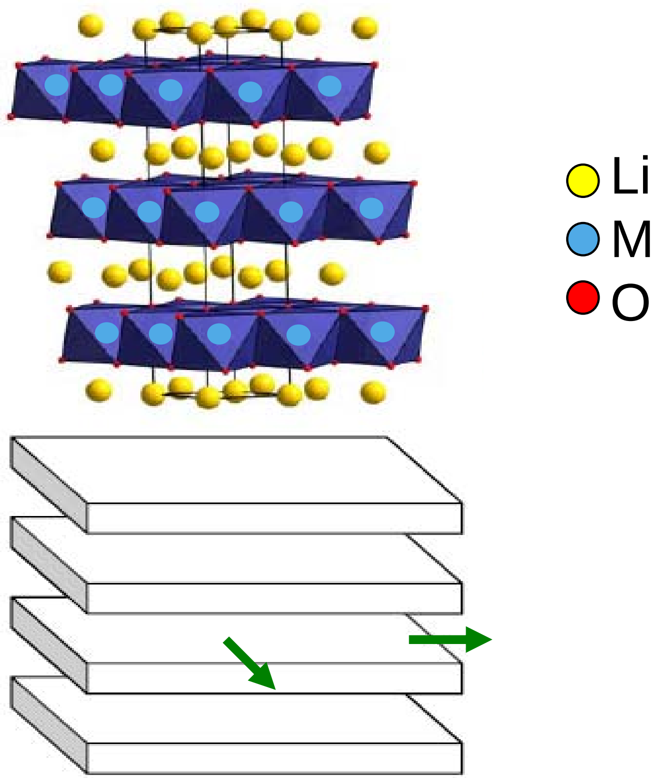

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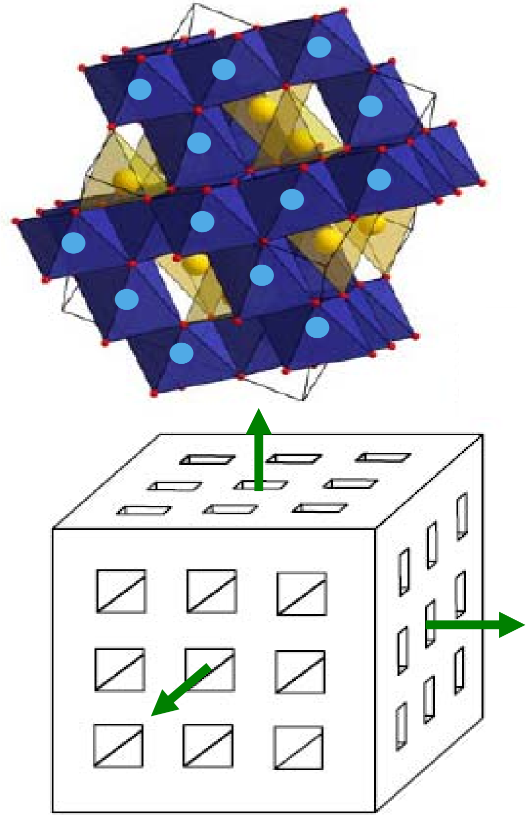

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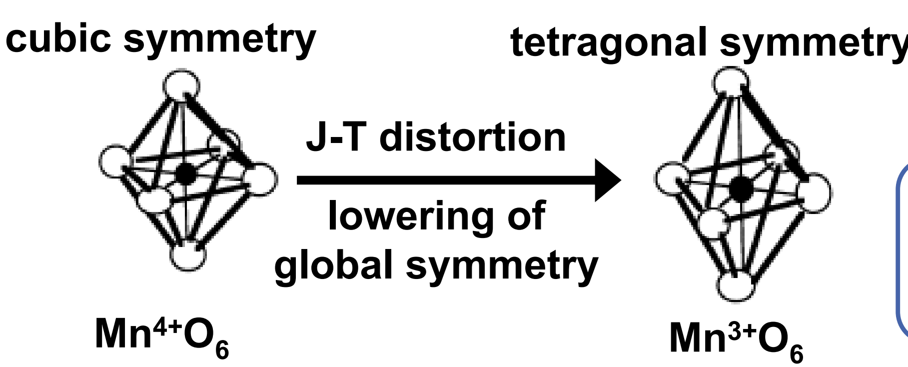
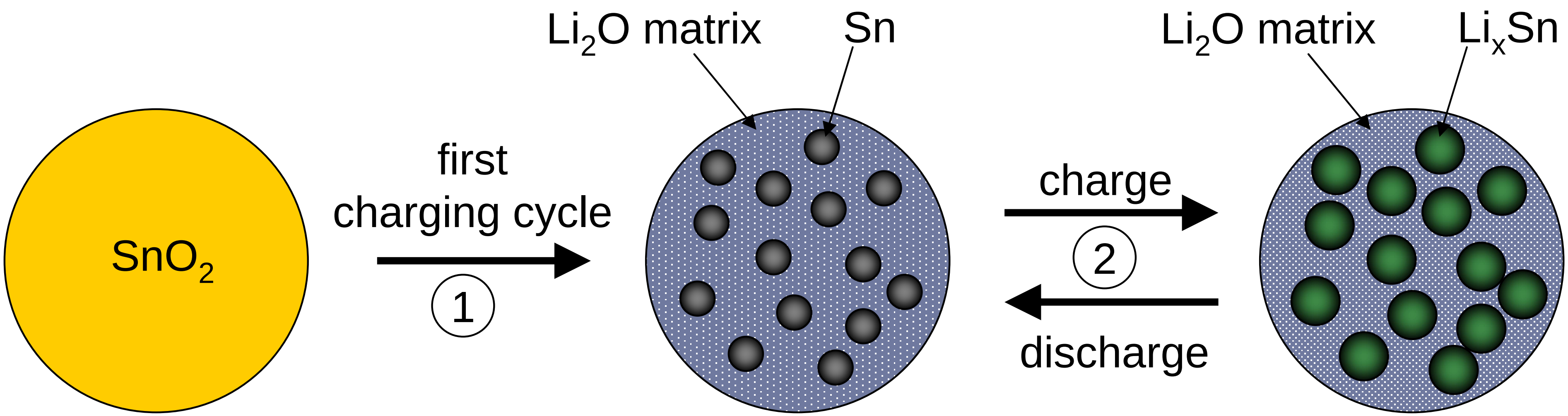


common cristallographic unit within the Mn-oxide lattice: MnO_6 octahedra

basics of SnO_2 as anode material



- during first charging cycle a Li_2O matrix is formed which compensates partly the huge volume change (up to 359%) of Sn
- reaction equation:

① $$SnO_2 + 4\,Li^+ + 4\,e^- \longrightarrow 2\,Li_2O + Sn$$

② $$Sn + x\,Li^+ + x\,e^- \longleftrightarrow Li_xSn$$

irreversible 4 Li/Sn
~700 mAh/g
reversible 4.4 Li/Sn
~800 mAh/g

summary and outlook

- r.f. magnetron sputtering was proved to be a powerful tool for deposition of $LiCoO_2$, Li-Mn-O and SnO_2 thin films on stainless steel and silicon substrates
- laser-induced formation of micro structures with high aspect ratios on thin films for enhancement of power density
- investigation of laser-annealing processes for adjustment of crystallinity and battery phases of $LiCoO_2$ and Li-Mn-O thin films
- evidence for desired battery phases through Raman and XRD analysis
- improvement of battery performance via laser modification of anodes and cathodes
- characterization of „solid electrolyte interface“ (SEI) on $LiMn_2O_4$

- further improvement of structuring processes (higher aspect ratios, sub-micron structures)
- further investigation of SEI on unstructured and structured anode/cathode materials