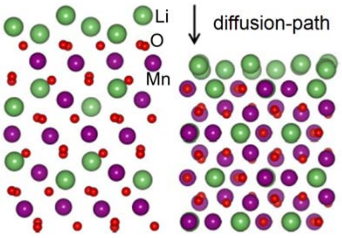
Karlsruhe Institute of Technology

IAM Institute for Applied Materials

Festkörper Dünnschicht Lithium-Ionen Batterien

S. Ulrich, J. Fischer, M. Strafela, K. Seemann, H. Leiste, M. Stüber, H.J. Seifert

Institute for Applied Materials (IAM), Department: Composites and Thin Films



Outline

- Introduction and motivation
- Components for thin film LIB
- All solid state thin film LIB
- Challenges in upscaling of all solid state thin film LIB
- Summary & outlook

VAKUUM-BESCHICHTUNG UND PLASMA-OBERFLÄCHENTECHNIK 2015

- **Introduction and motivation**
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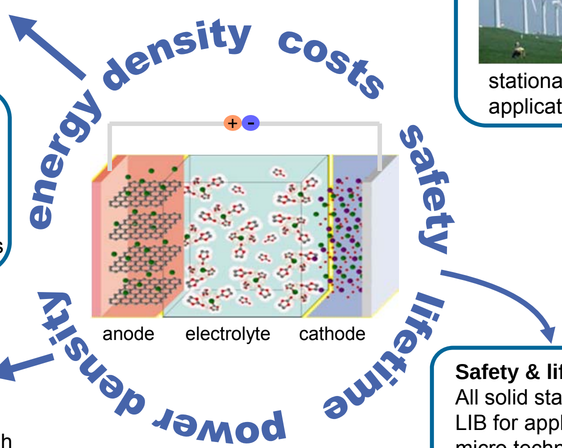
Introduction and motivation

Energy density

- "how much energy is stored"
- defined by the material used


stationary applications


automotive applications

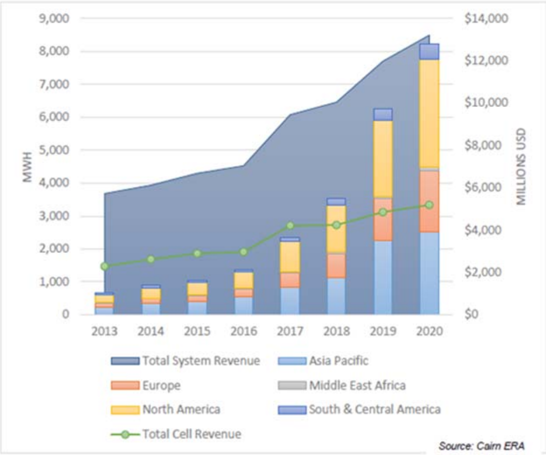


Power density

- "how fast is the energy accessible"
- defined by lithium diffusion rate
- is increased with high surface area

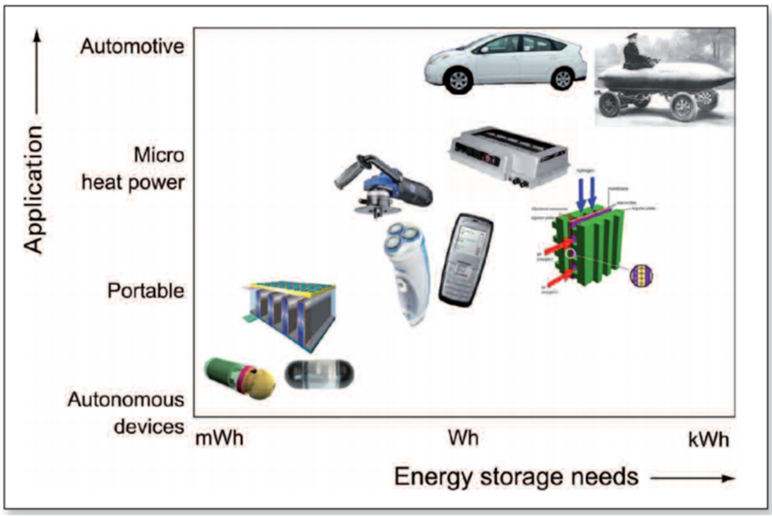
Safety & lifetime
All solid state thin film LIB for applications in micro technology

Global Stationary Storage Battery Energy Capacity by Region in MWH and Cell and System Revenue in Millions of USD Forecast: 2013-2020



Quelle: Jaffe, Sam: Battery Systems for Stationary Storage, URL: http://www.sdle.co.il/AllSites/810/Assets/cairn%20era%20battery%20systems%20for%20stationary%20storage%20summary%20and%20list%20of%20charts%20and%20figures.pdf (zuletzt Abgerufen am: 7.10.2015)

Energy storage needs by Application

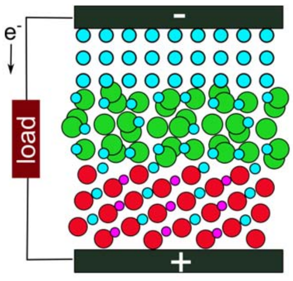


Quelle: Peter H.L. Notten: 3D-integrated all-solid-state batteries, URL: http://www.europhysicsnews.org/articles/epn/pdf/2011/03/epn2011423p24.pdf (zuletzt Abgerufen am: 7.10.2015)

Introduction and motivation
All solid state thin film cells

Properties:

- stability at high cell voltages
- nearly no side reactions
- low self discharge rates
- not flammable
- high reversibility
- high temperature operation (up to 180°C)



schematic drawing:
„Thin film micro-batteries“ Nancy J. Dudney;
The Electrochem. Society *Interface 2008*

Applications for all sold state thin film LIB

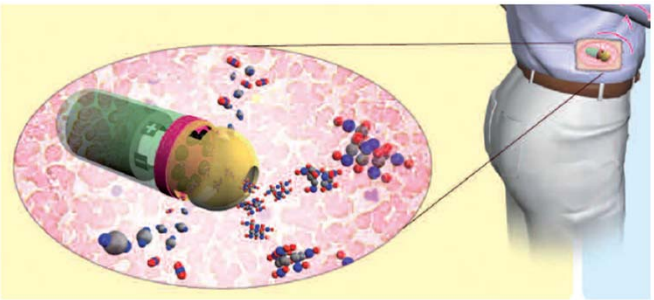
- **Smart cards**
- **Radio frequency identification (RFID)**
- **Implantable medical devices**
  - Cochlear implantats
  - Neurosimulators
- **Semiconductors, integrated circuits**
  - non-volontile SRAM, flash RAM
  - mobile and personal devices
  - cellular telephony
  - personal digital assistance (PDA)
- **Energy autarc sensor devices**
- **Sensors for tool coating**
- **Micro and nanotechnology**
- **Aicraft space applications**
  - **12000€/kg spaceliftcosts** (http://www.esa.int/ger/ESA_in_your_country/Germany/Erfolgsstory_Raumtransport_Wie_Phoenix_aus_der_Asche)

Source: Aveso Displays

RFID - Sensor

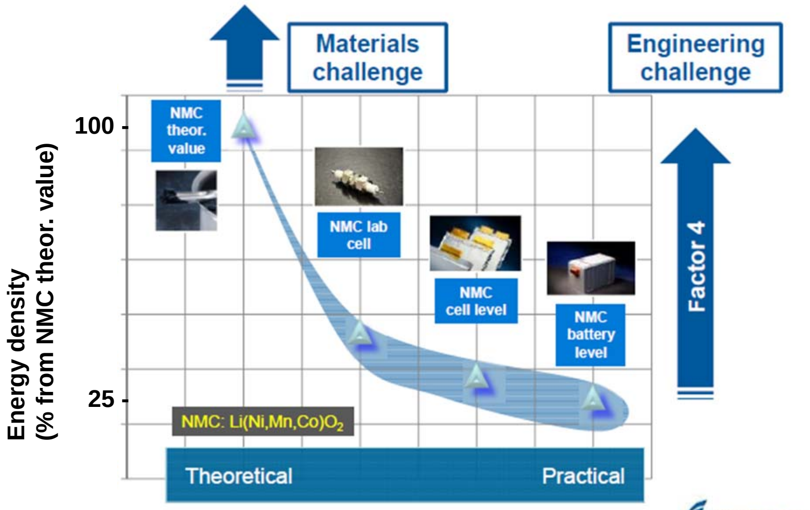
Source : PolyIC

Mikrosysteme in der Medizintechnik: Schematische Darstellung einer Mikropille, die automatisch zu definierten Zeitpunkten Wirkstoffe abgibt



Quelle: Peter H.L. Notten: 3D-integrated all-solid-state batteries, URL: http://www.europhysicsnews.org/articles/epn/pdf/2011/03/epn2011423p24.pdf (zuletzt Abgerufen am: 7.10.2015)

Theoretical and practical energy density

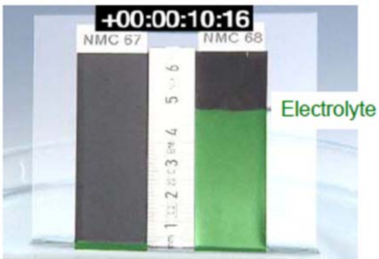


Values for NMC from: http://msdssearch.dow.com

Surface modification: electrolyte filling

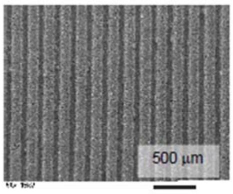
KIT Karlsruhe Institute of Technology

Major result: Time for electrolyte filling can be reduced from 24 hours to few minutes by structuring of electrodes without affecting specific capacity



Unstructured NMC-electrode | Laser-structured NMC-electrode

Electrode surfaces with micro-structured channels



by laser-structuring

by calandering

W. Pfleging, et al., WO 2012/139553 (2012)

HELMHOLTZ ASSOCIATION

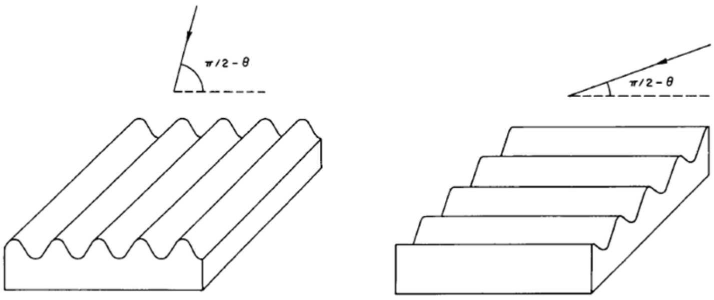
Surface modification by thin film technology

KIT Karlsruhe Institute of Technology

Theory of ripple topography induced by ion bombardment

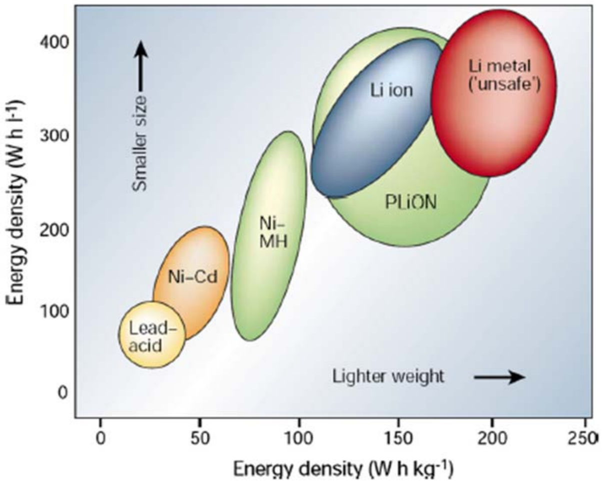
R. Mark Bradley
Department of Physics, Colorado State University, Fort Collins, Colorado 80523
James M. E. Harper
IBM T. J. Watson Research Center, Yorktown Heights, New York 10598

2390 J. Vac. Sci. Technol. A 6 (4), Jul/Aug 1988



See also: Novel techniques for modifying microtube surfaces with various periodic structures ranging from nano to microscale
J. Vac. Sci. Technol. B 31, 011806 (2013)

Comparison of the different batteries in terms of volumetric and gravimetric energy density



J.M. Tarascon, M. Armand, Nature 414 (2001) 359–367
See also: C. Liang, M. Gao, H. Pan, Y. Liu, M. Yan, J. Alloy 575 (2013) 246-256

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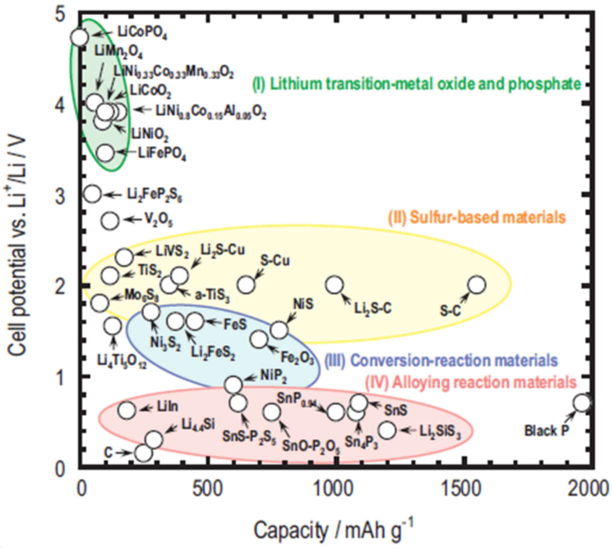
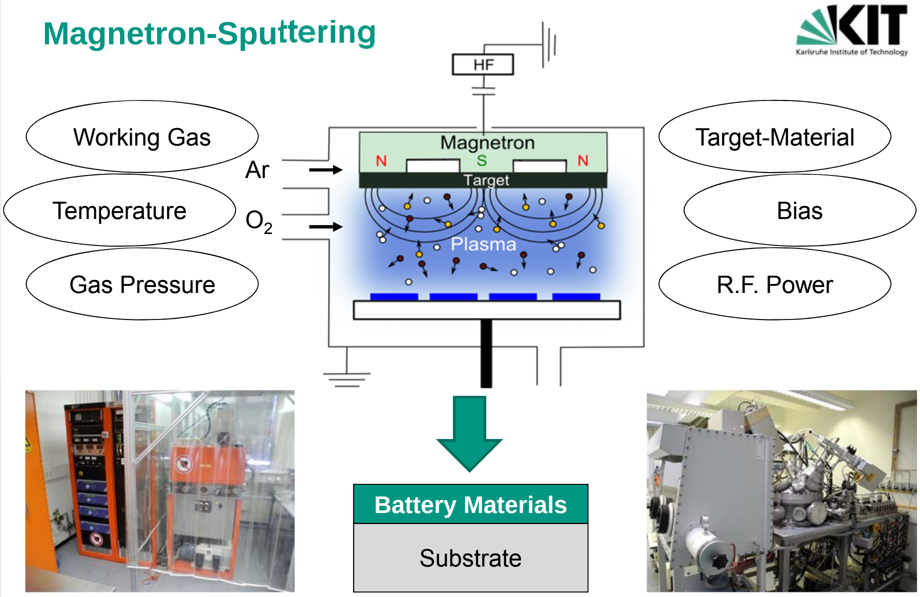
Cell potential (vs. Li+ /Li) and reversible capacity (per gram of active material) in all-solid-state cells

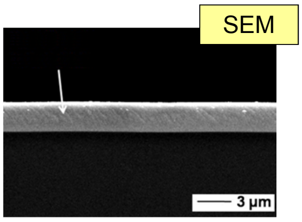


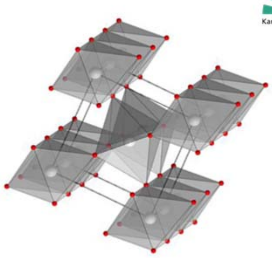
Masahiro Tatsumisago, Motohiro Nagao, Akitoshi Hayashi
Journal of Asian Ceramic Societies
1 (2013) 17–25

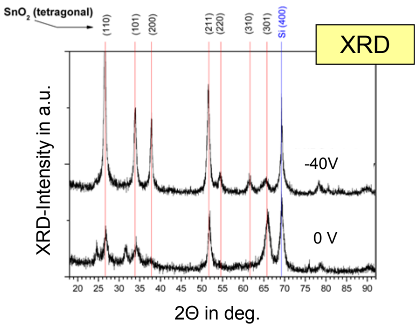
Magnetron-Sputtering

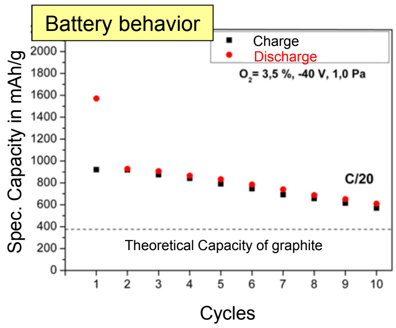


Thin Film Anode: SnO_2



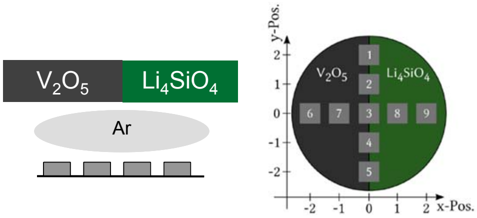




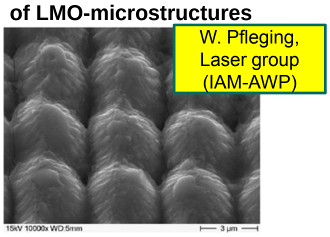


Thin Film Solid-State-Electrolyte: LVSO

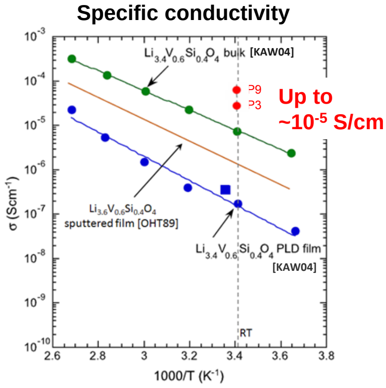
Materials research by a combinatorial segmented ceramic target arrangement



LVSO-deposition on top of LMO-microstructures



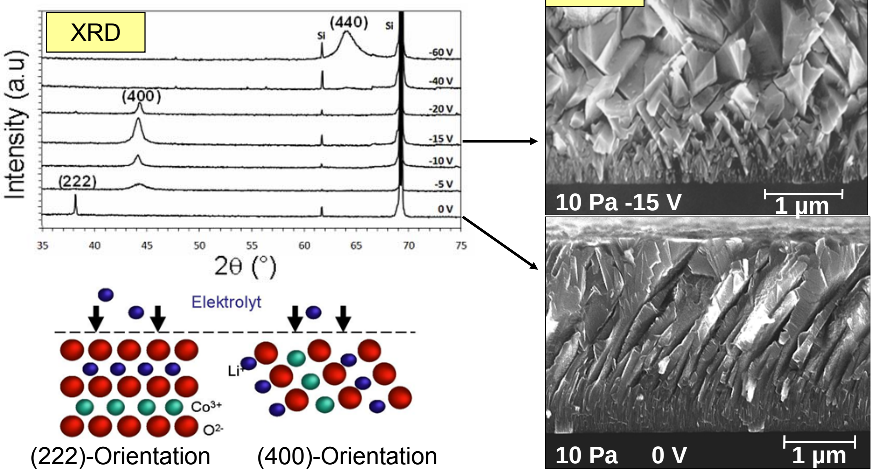
Specific conductivity



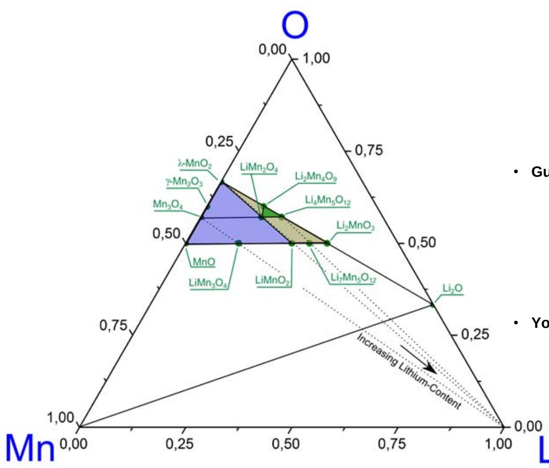
[OHT89] H. Ohtsuka et al., Jpn. J. Appl. Phys. ***28*** *(1989) 2264*
[KAW04] J. Kawamura, et al., Solid State Ionics ***175*** *(2004) 273*

Thin Film Cathode: $LiCoO_2$

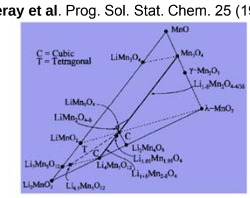
Variation of the Substrate-Bias at 10,0 Pa



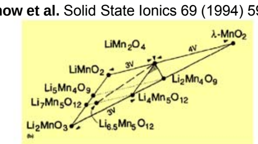
Ternary System Li-Mn-O



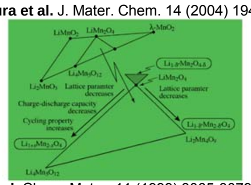
- **Thackeray et al**. Prog. Sol. Stat. Chem. 25 (1997) 1-71.



- **Gummow et al.** Solid State Ionics 69 (1994) 59-67.

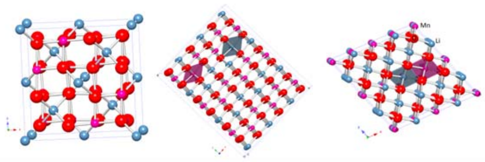


- **Yonemura et al.** J. Mater. Chem. 14 (2004) 1948-1958.



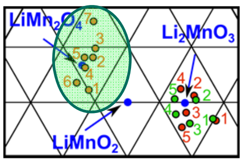
- **Dahn et al.** Chem. Mater. 11 (1999) 3065-3079.
- **Cupid, Seifert et al.** J. Mater. Sci. 48 (2013) 3395-3403

Li - Mn - O: Structures and Properties



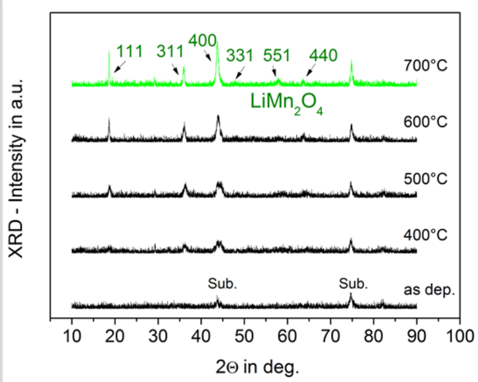
Stoichiometric Composition	c-$LiMn_2O_4$	o-$LiMnO_2$	m-Li_2MnO_3
Crystal System	cubic	orthorhombic	monoclinic
Space Group	Fd-3m (227)	Pmmn (59)	C2/m (12)
Density	4.29 g/cm^3	4.22 g/cm^3	3.88 g/cm^3
Specific gravimetric Capacity (theoretical)	148 mAh/g	285 mAh/g	459 mAh/g
Specific gravimetric Capacity (in practice)	80 - 135 mAh/g	120 - 180 mAh/g	150 - 250 mAh/g
Average Manganese Oxidation State (Stoichiometric Phase)	$Mn^{+3,5}$	$Mn^{+3,0}$	$Mn^{+4,0}$
Intercalation and Deintercalation Plateaus of Li^+	~ 4.0 V	~ 4.0 V / ~3.0 V	~ 3.0 V / ~4.0 V / ~4.5 V
Lattice Parameter	a = 0.8240 nm	a = 0.2805 nm b = 0.5757 nm c = 0.4572 nm	a = 0.4937 nm b = 0.8532 nm c = 0.5030 nm

1 c-$LiMn_2O_4$ - Spinel

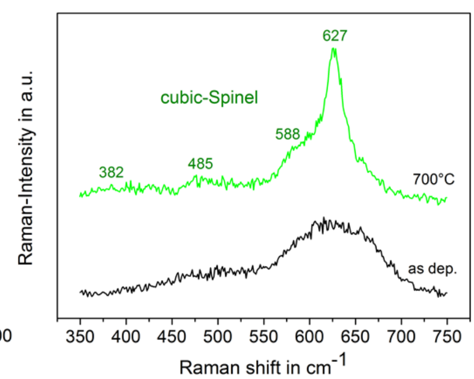


$LiMn_2O_4$-target, 100 W, r.f., 16 Pa, Ar
Annealing: 700°C, 30 min, air

XRD

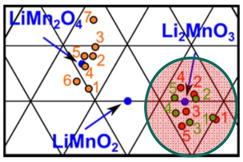


Raman

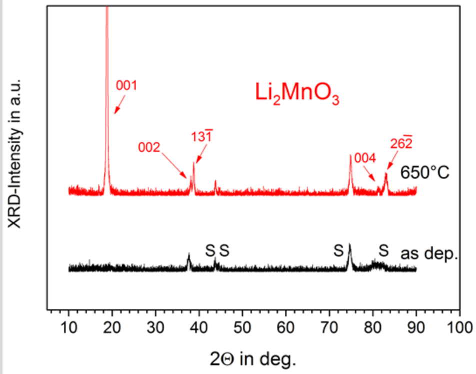


2 m-Li_2MnO_3

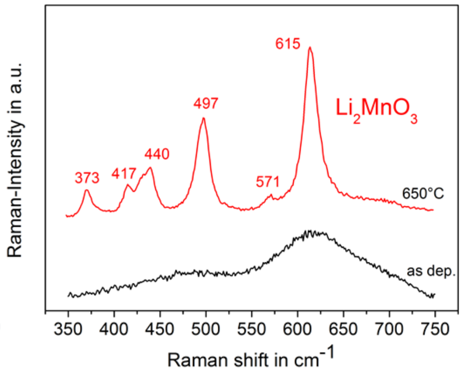
Li_2MnO_2-target, 100 W, r.f., 4 Pa, Ar
Anealing: 650°C, 60 min, air



XRD

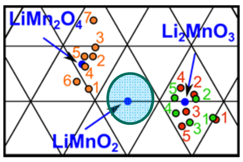


Raman

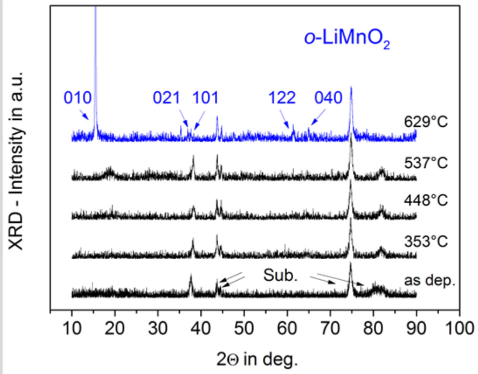


3 o-$LiMnO_2$

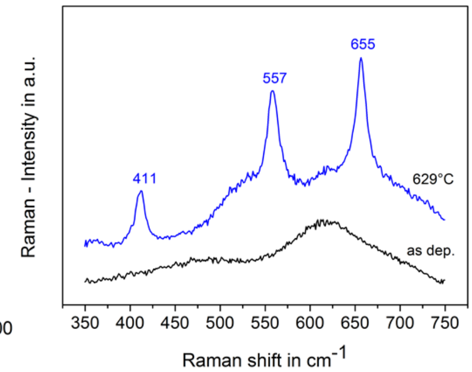
Li_2MnO_2-target, 100 W, r.f., 4 Pa, Ar
Anealing: 650°C, 60 min, vacuum



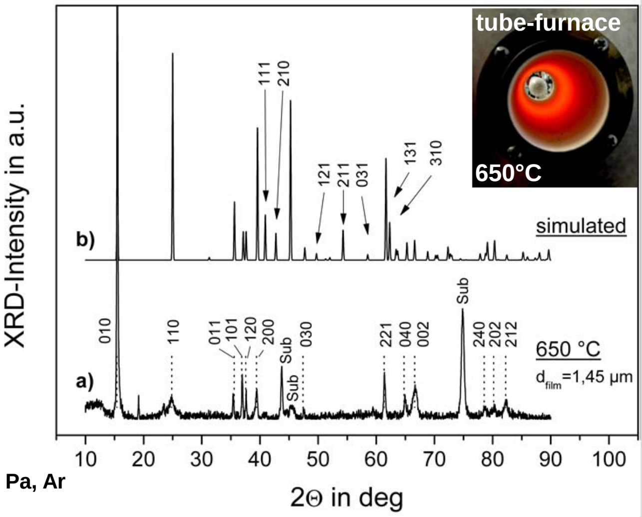
XRD



Raman

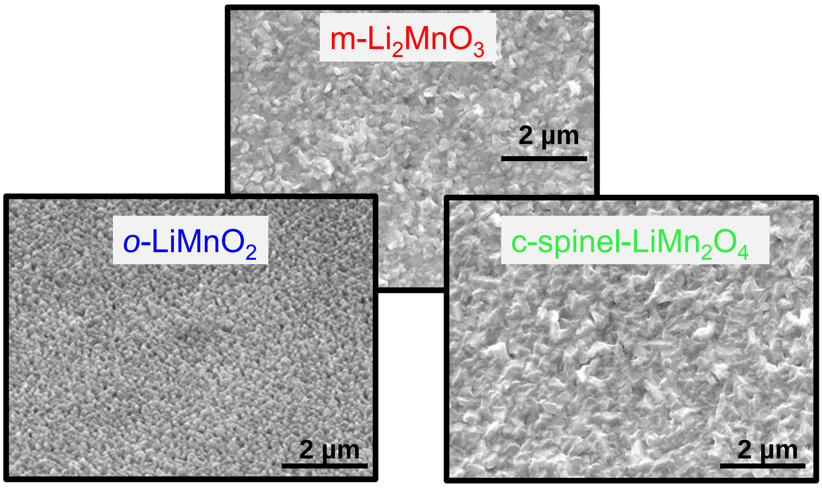


Microstructure: TEM & XRD: o-$LiMnO_2$



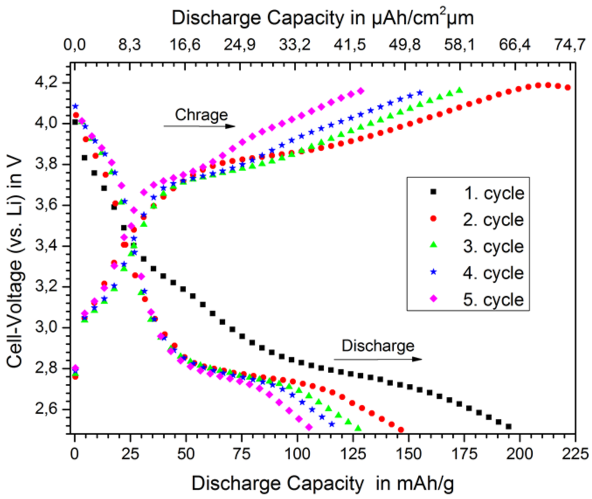
Li_2MnO_2-target, 100 W, r.f., 4 Pa, Ar
Anealing: 650°C, 60 min, air

SEM- investigations



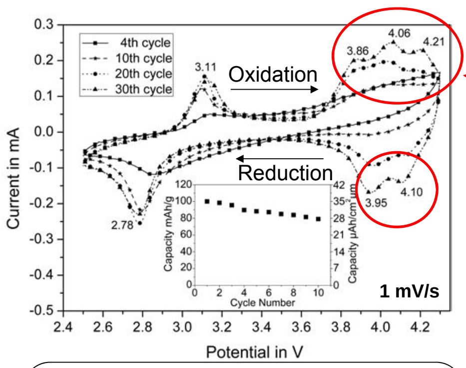
- **High surface qualities**
- **Different surface topographies**

Electrochemical Characterization 1: o-$LiMnO_2$



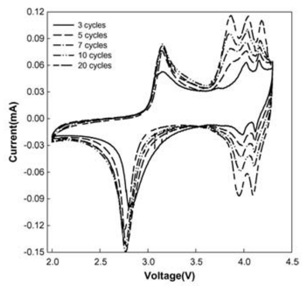
Swagelok Assembly:
Anode: Lithium Ribbon
Separator:
Glass Fiber Filter
Electrolyte:
$LiPF_6$ EC/DMC (1:1)

Electrochemical Characterization 2: o-$LiMnO_2$



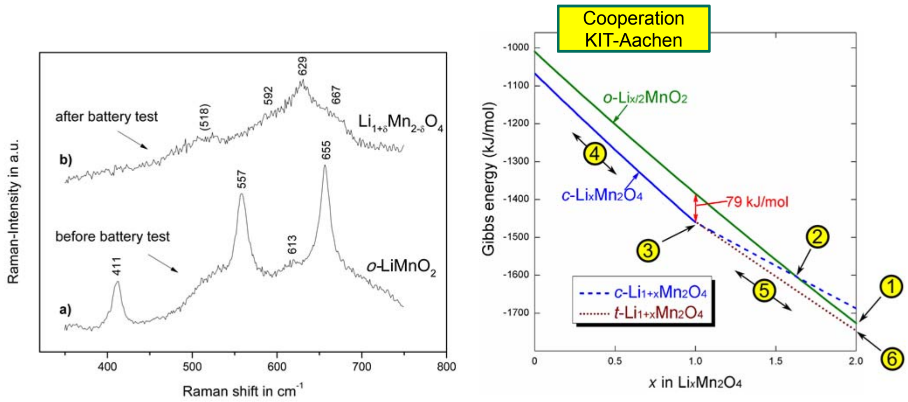
Increasing Redox-Signals around 3.95 V und 4.1 V indicate a Cycle induced Transformation into the Spinel Structure.

- **4 V - region: Lithium intercalation and deintercalation from the tetrahedral sides of the cubic spinel**
- **3 V - region: Induced transformation from the cubic to a tetragonal phase (Jahn-Teller-Distortion)**



Jin et al. Journal of Power Sources 189 (2009) 620–623

Post-mortem-Analysis after Batterytest



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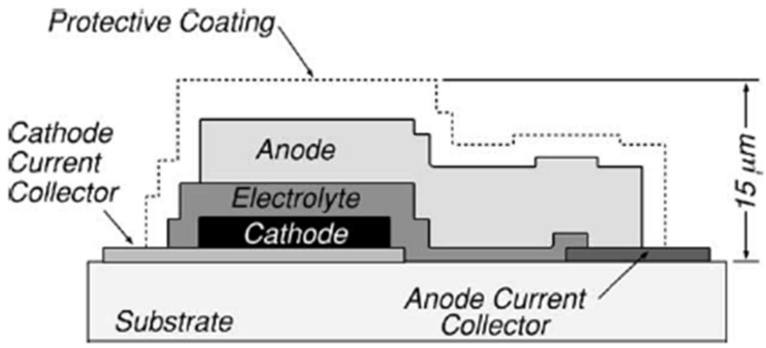
Design of all solid state thin film Li (ion) batteries



Materials Science and Engineering B 116 (2005) 245–249

Solid-state thin-film rechargeable batteries

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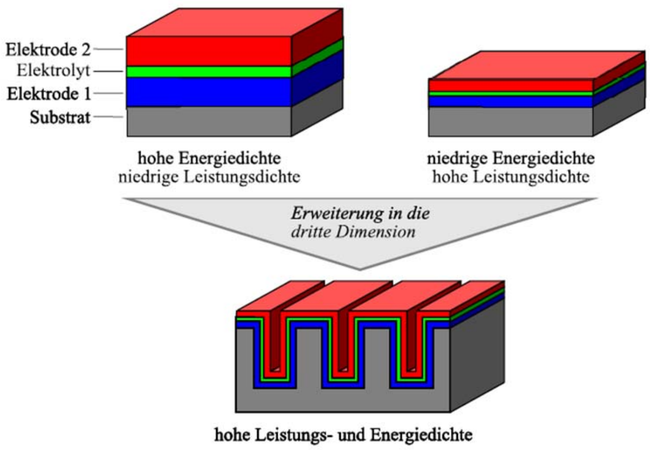
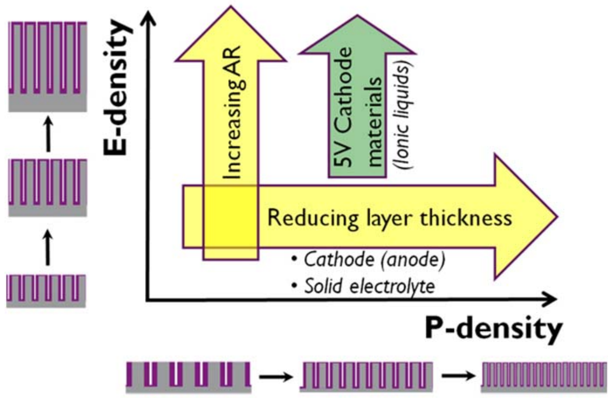
www.elsevier.com/locate/mseb

Erhöhung der Leistungs- wie auch Energiedichte pro projizierter Grundfläche durch dreidimensionalen Aufbau der Batterie



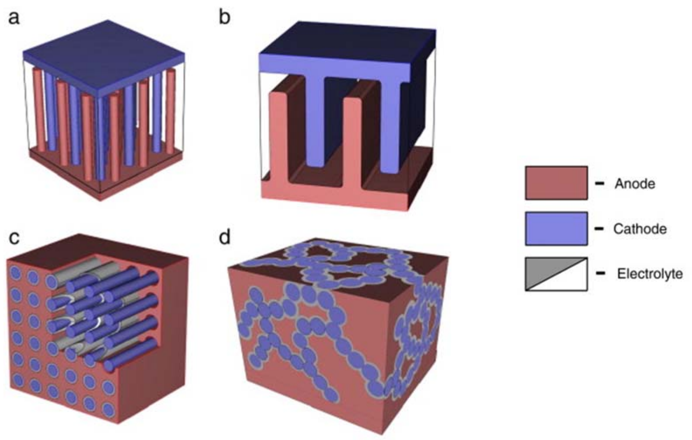
Quelle: Laura Hannele Bohne: Integrierte 3D-Lithium-Ionen-Dünnschichtbatterien: Dünnschichtkathoden auf strukturierten Substraten und elektrochemische Eigenschaften URL: http://tuprints.ulb.tu-darmstadt.de/2957/1/Dissertation_LB_web.pdf (zuletzt Abgerufen am: 7.10.2015)

scaling the film thickness of the functional battery layers and the aspect ratio of the 3D architectures



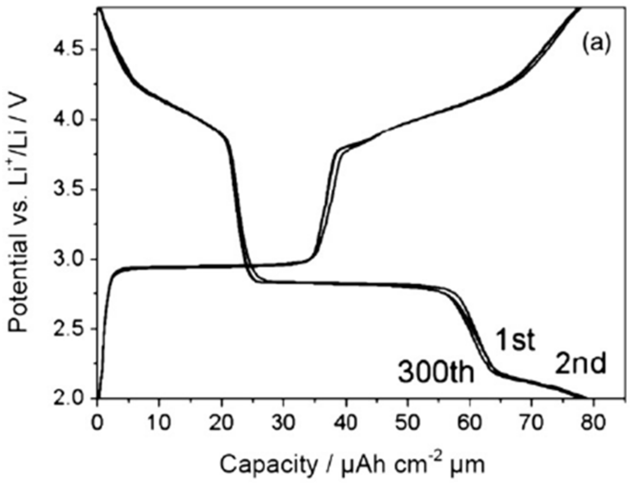
Quelle: ohne Autor: 3D thin-film storage devices , URL: http://www.imec.be/ScientificReport/SR2010/2010/1159137.html (zuletzt Abgerufen am: 7.10.2015)

Schematische Darstellung unterschiedlicher Ansätze für 3D-Batterien: (a)–(c) regelmäßig strukturierte Elektroden (d) schwammartige Elektroden



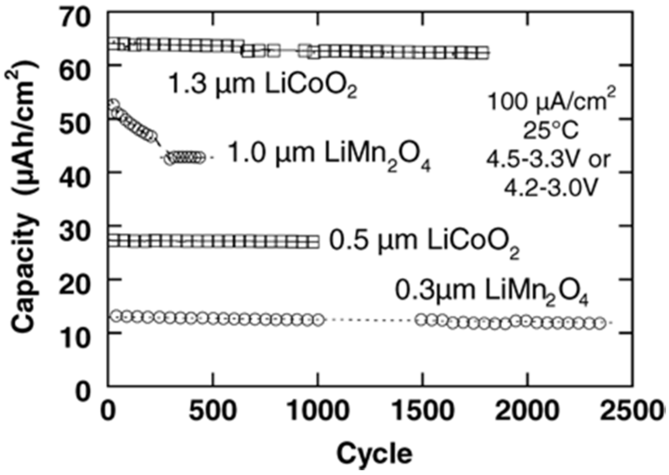
Quelle: Vahur Zadin: Finite element modelling of ion transport in the electrolyte of a 3D-microbattery, URL: http://www.sciencedirect.com/science/article/pii/S016727381000069X (zuletzt Abgerufen am: 7.10.2015)

Voltage composition profiles of $LiMn_2O_4$/LiPON/Li



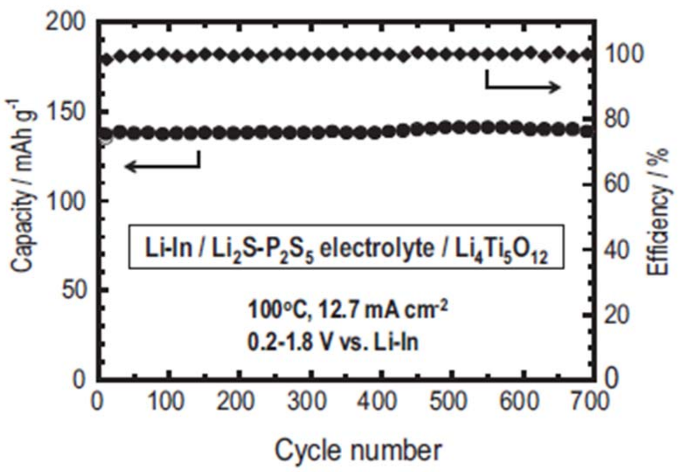
S. Jacke, J. Song, G. Cherkashinin, L. Dimesso, W. Jaegermann, Ionics 16 (2010) 769

High cycle stability of all solid state thin film lithium batteries



N.J. Dudney / Materials Science and Engineering B 116 (2005) 245–249

Cycle stability for all solid state thin film LIB

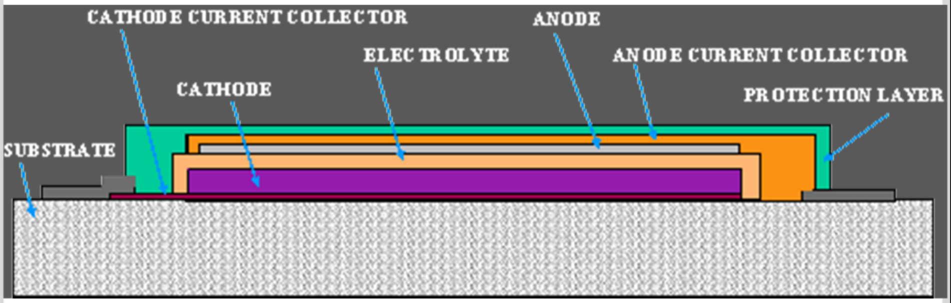


M. Tatsumisago, M. Nagao, A. Hayashi, Journal of Asian Ceramic Societies 1 (2013) 17–25

Design of all solid state thin film Li (ion) batteries

cathodes: $LiCoO_2$, $LiMnO_2$, V_2O_5
solid state electrolyte: LiPON
anode: Sn_3N_4, Li

total thickness: less than 5 µm
tickness of cathode and anode: 0.3 µm
temperature range: -40°C up to 150 °C

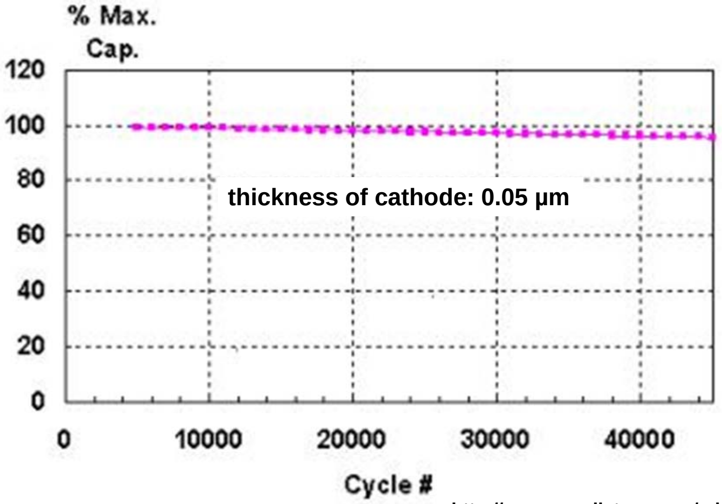


intrinsically safe
high temperature performance
long cycle life

flexible substrates usable
high specific power and energy density
high rate capability

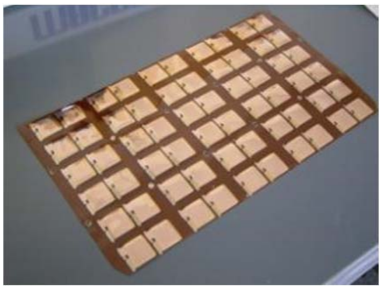
http://www.excellatron.com/advantage.htm

High cycle stability of all solid state thin film lithium batteries



http://www.excellatron.com/advantage.htm

Polymer substrates and pouch cells of all solid state thin film lithium (ion) batteries



http://www.excellatron.com/advantage.htm

Properties of all solid state thin film LIB

Nominal Capacity	1 mAh (0.1 mAh, 0.5 mAh, 1 mAh, 10mAh)
Dimension (T x W x D)	5cm x 3.8 cm x 0.037 cm
Storage temperature	-40 to 150ºC
Operating Temperature	-40 to 150ºC
Discharge rate	> 10C at 20ºC > 500C at 150ºC
Cyclability	< 10% capacity loss in 1,000 cycles at 20ºC < 10% capacity loss in 100 cycles at 150ºC

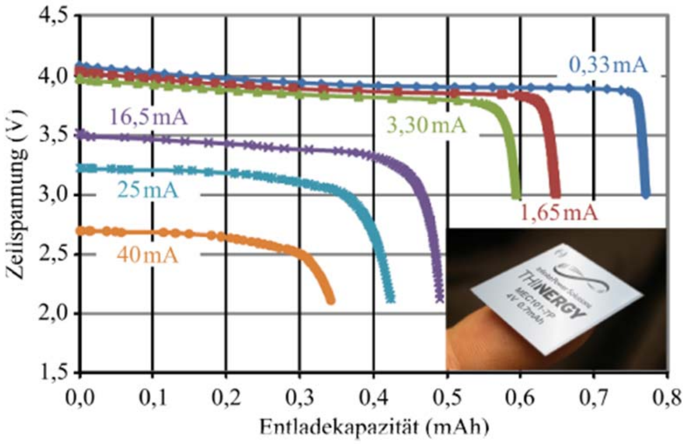
http://www.excellatron.com/advantage.htm

Comparison of battery performances

Battery Type	Specific Energy (Wh/kg)	Energy Density (Wh/l)	Specific Power (W/kg)	Cycle Life
Nickel Cadmium	40	100	400	400
Nickel Metal Hydride	90	245	180	600
Lithium ion (liquid electrolyte)	155	410	300	500
Lithium Polymer	180	380	360	500
Thin Film Li-ion	250	1,041	2,500	1,000
Thin Film Li	300	959	6,000	40,000

http://www.excellatron.com/advantage.htm

Kommerziell erhältliche Dünnschicht-festkörperbatterie THINERGY MEC101-7P von Infinite Power Solutions



Quelle: Laura Hannele Bohne: Integrierte 3D-Lithium-Ionen-Dünnschichtbatterien: Dünnschichtkathoden auf strukturierten Substraten und elektrochemische Eigenschaften URL: http://tuprints.ulb.tu-darmstadt.de/2957/1/Dissertation_LB_web.pdf (zuletzt Abgerufen am: 7.10.2015)

THINERGY MEC200-Serie von Infinite Power Solutions

Merkmale	Anwendungen
•Schmaler Formfaktor - 170 µm dick •Kapazitätsoptionen sind von 130 µAh bis 2,2 mAh verfügbar •Komplette Festkörper-Bauweise •Fähigkeit für hohe Entladerate •Extrem geringe Selbstentladerate •Branchenführende Lebensdauer •Schnelles Aufladen •Umweltfreundlich/sicher	•Lösungen für Energieernte/netzunabhängige Systeme •Remote-/autonome, drahtlose Sensoren •Speicher- und Echtzeituhr (RTC)-Sicherung •Semiaktive RFID-Transponder •Smart Cards (etwa Einheiten mit Display/biometrischen Daten) •Medizinische Geräte •Hochtemperaturanwendungen •Militär/Verteidigungsministerium und Luftfahrt

Quelle: ohne Autor: THINERGY MEC200-Serie URL: http://www.digikey.de/product-highlights/de/de/infinite-power-solutions-thinergy-mec200/1775 (zuletzt Abgerufen am: 8.10.2015)

Infinite Power Solutions,Inc.

THINERGY

Solid-State, Rechargeable, Micro-Energy Cells (MECs)

	Units	MEC225	MEC220	MEC201	MEC202
Open Circuit Voltage (OCV)	V	4.1	4.1	4.1	4.1
Package Size/Footprint [1]	in. mm	0.5 x 0.5 12.7 x 12.7	1.0 x 0.5 25.4 x 12.7	1.0 x 1.0 25.4 x 25.4	1.0 x 2.0 25.4 x 50.8
Package Thickness	in. mm	0.007 0.17	0.007 0.17	0.007 0.17	0.007 0.17
Typical Internal Resistance	Ω	260	120	45	20
Maximum Continuous Current	mA	7	15	40	90
Nominal Capacity Options	mAh	0.13	0.3 0.4	0.7 1.0	1.7 2.2
Equivalent Energy in Joules	J	1.8	4 5.5	10 14	24 32
Typical Recharge Time to 90% (at 4.1V CV)	Min.	15	15	15	15
Operating Temperature Range	°C	-40 to +85	-40 to +85	-40 to +85	-40 to +85
Operating/Shelf Life	Years	>15	>15	>15	>15
Recharge Cycles [2]		100,000	100,000	100,000	100,000
Typical Charge Loss/Year		2%	2%	2%	2%
Supersedes [3]		MEC125	MEC120	MEC101	MEC102

Quelle: ohne Autor: Infinite Power Solutions,Inc. URL: http://www.cytech.com/products-ips (zuletzt Abgerufen am: 8.10.2015)

- Introduction and motivation
- Components for thin film LIB
- All solid state thin film LIB
- **Challenges in upscaling of all solid state thin film LIB**
- Summary & outlook

Challenges in upscaling of all solid state thin film LIB

- Clean room technology
- No humidity conditions
- No pinholes conditions
- Due to substrate transport: no substrate bias, no external heating
- Processing of insolating coatings
- Large increase of growth rate
- Sputter/Evaporation of pure lithium
- Reactive Processes
- Multilayer design (thin thickness of components, 50 nm)

- Introduction and motivation
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Summary

All solid state thin film lithium (ion) batteries

showing the **highest cycle stability** and **safety**

and are the best choice for applications in **micro system technology**.

Improvement of growth rate and **upscaling** are necessary in order

to **reduce costs** an **increase energy density.**

Enhancement of ion conductivity and **electrical breakdown voltage**

in **solid state electrolytes** is needed for an increase of **power density**.

Thank you very much for your attention,

thanks for the invitation

and to my whole team in Karlsruhe!