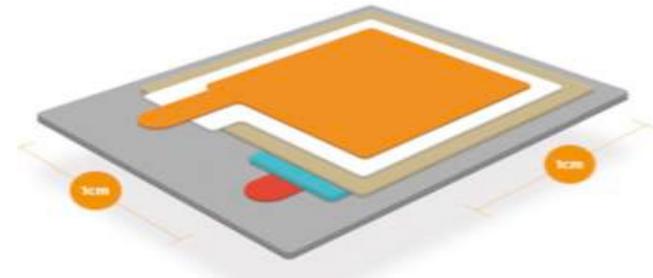
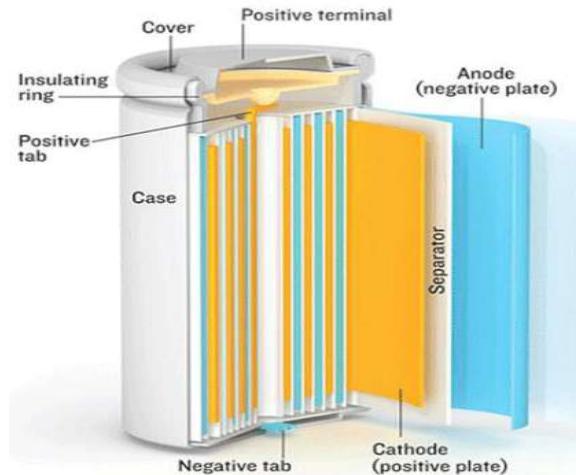


Lithium-ion batteries: finally a Nobel Prize, but how about the future?

Prof. dr. ir. Mark Huijben



2019 Nobel Prize in Chemistry

"for the development of lithium-ion batteries."



John B. Goodenough



M. Stanley Whittingham



Akira Yoshino

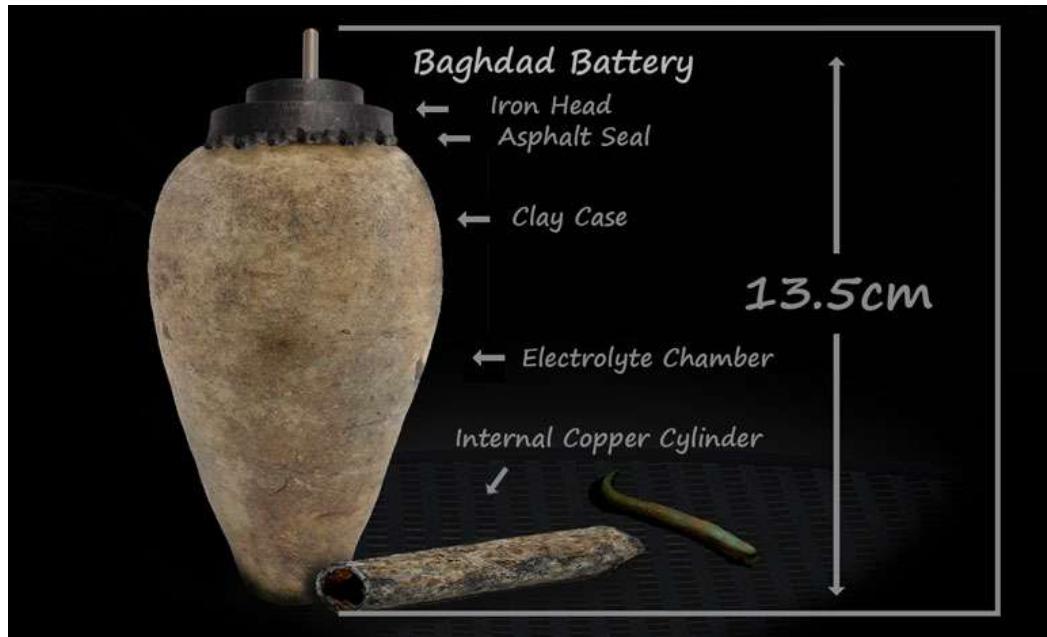


1800 : Inventor of the battery, Alessandro Volta



“Baghdad” Batteries (~1000-2000 years ago).

Terracotta jars containing a copper cylinder separated from an iron rod by a non-conductive stopper, and filled with an electrolyte.



Battery technologies

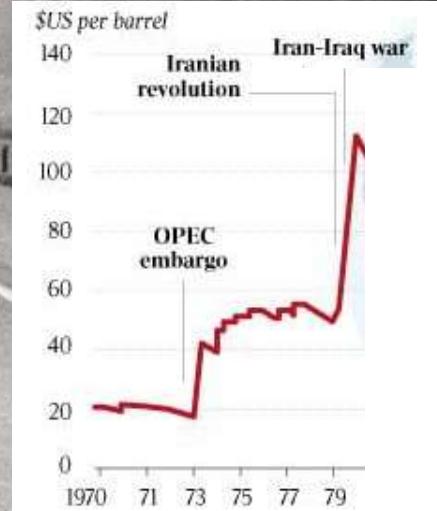


NOT rechargeable !



1970's : Oil crisis

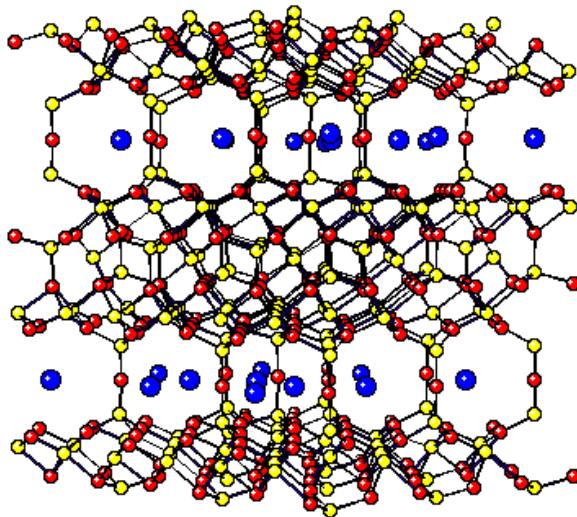
More interest into new rechargeable batteries



Netherlands, a Sunday in 1973

1967 Discovery of high ionic conductivity in Sodium Beta-Alumina

$11 \text{ Al}_2\text{O}_3 - x \text{ Na}_2\text{O}$ (with $x = 1.0 - 1.6$)

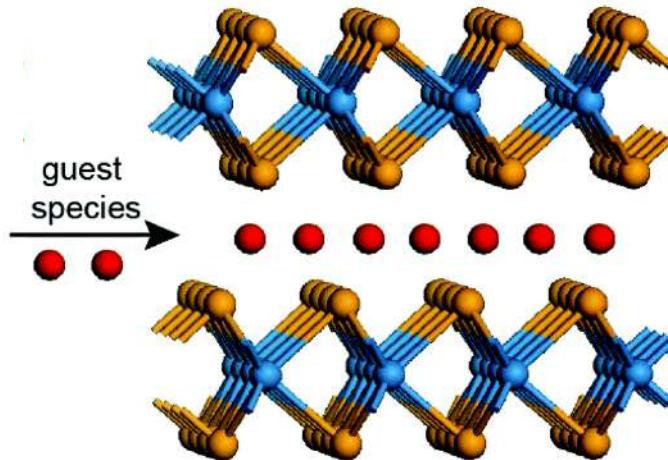


Y. Y. Yao and J. T. Kummer,
Ion exchange properties of and rates
of ionic diffusion in beta-alumina,
J. Inorganic Nuclear Chem. 29,
2453–2466, 1967.



Intercalation

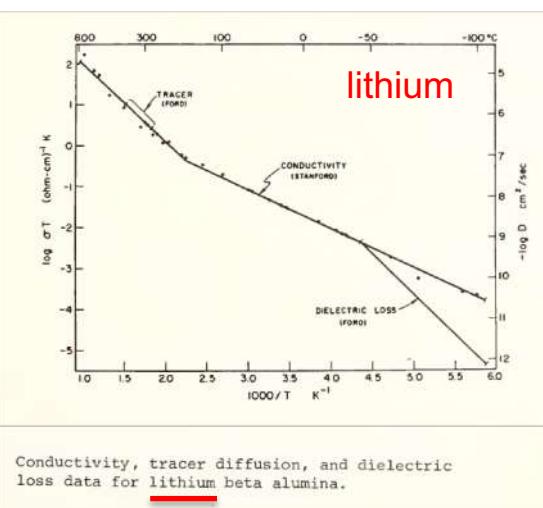
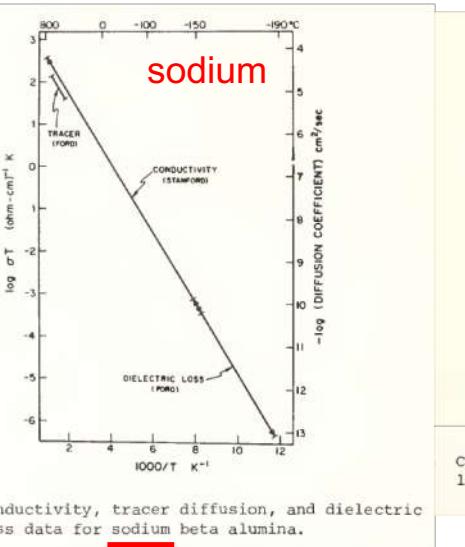
is the reversible insertion of an ion or a molecule into a crystalline lattice without any significant change of that lattice except for a minor expansion or contraction.



BETA ALUMINA - PRELUDE TO A REVOLUTION IN SOLID STATE ELECTROCHEMISTRY

M. S. Whittingham and R. A. Huggins

Department of Materials Science and Engineering
Stanford University
Stanford, California 94305



Intercalation Complexes of Lewis Bases and Layered Sulfides: A Large Class of New Superconductors

F. R. Gamble¹, J. H. Osiecki¹, M. Cais¹, R. Pisharody¹, F. J. DiSalvo², T. H. Geballe²

¹Syva Research Institute, Palo Alto, California 94304

²Stanford University, Stanford, California 94305

Science 174, 493–497 (1971)

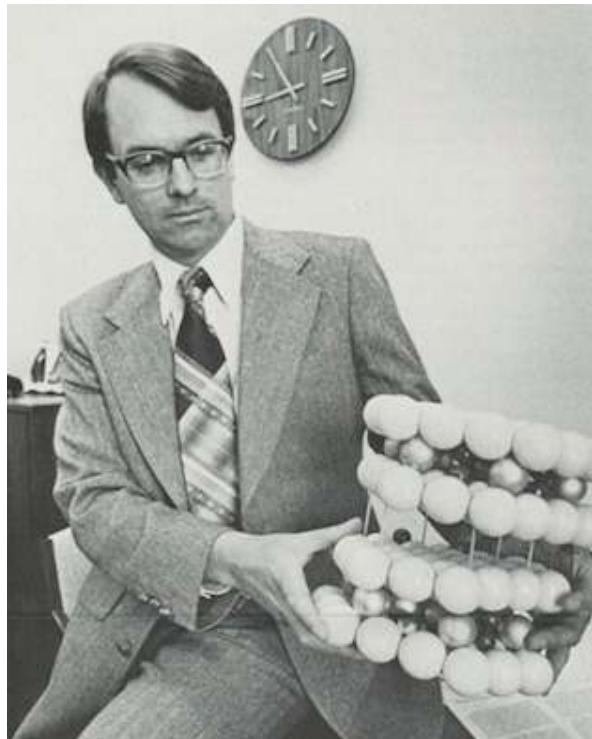


Bell Laboratories

EXXON



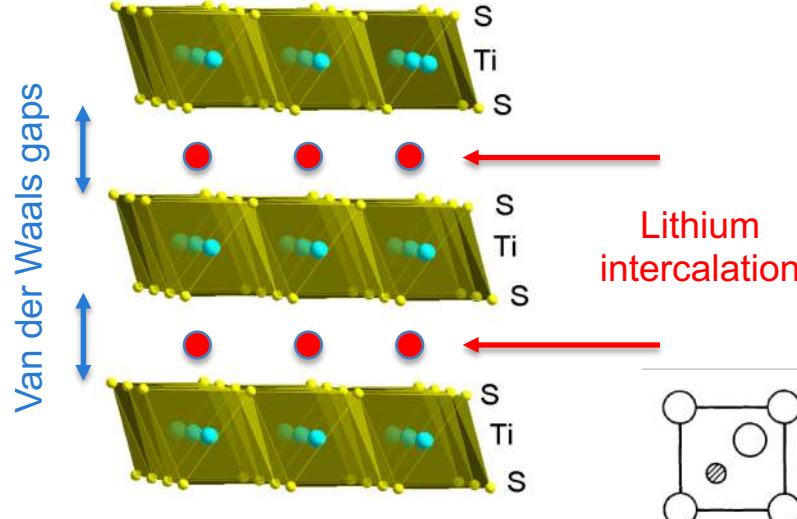
1975 Discovery of lithium intercalation into TiS_2



M. Stanley Whittingham

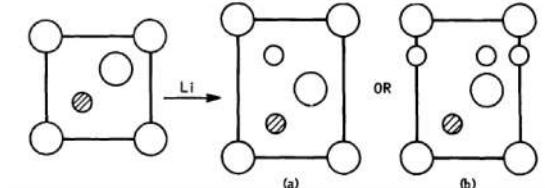
THE LITHIUM INTERCALATES OF THE TRANSITION METAL DICHALCOGENIDES

M. Stanley Whittingham and Fred R. Gamble Jr.
Corporate Research Laboratory
Exxon Research and Engineering Co., Linden, NJ 07036

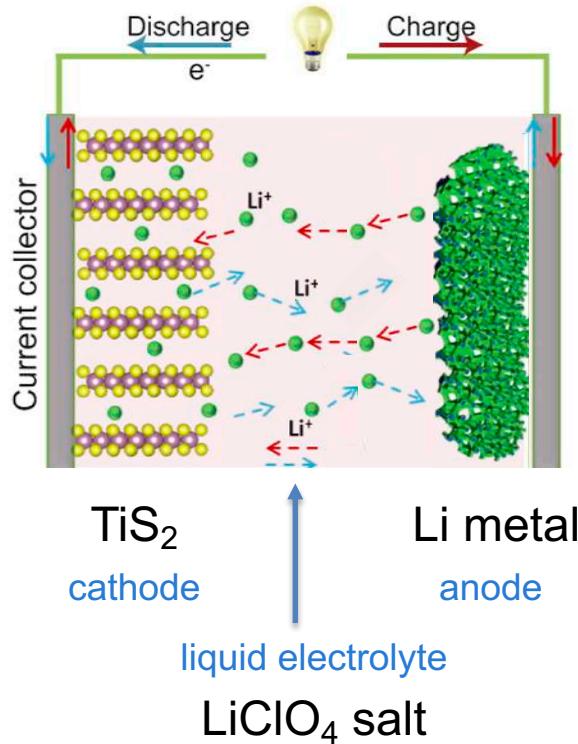


MRS bulletin 10, 363 (1975)
Prof. Mark Huijben, University of Twente

	a	c
TiS_2	3.407	1 x 5.696
ZrS_2	3.665	1 x 5.835
HfS_2	3.635	1 x 5.856
NbS_2	3.34	3 x 6.00
TaS_2	3.340	2 x 6.04
MoS_2	3.16	2 x 6.15
WS_2	3.16	2 x 6.18
TiSe_2	3.535	1 x 6.004
ZrSe_2	3.776	1 x 6.160
HfSe_2	3.742	1 x 6.160
VSe_2	3.35	1 x 6.10
NbSe_2	3.45	2 x 6.27
TaSe_2	3.436	2 x 6.348
MoSe_2	3.30	2 x 6.50
WSe_2	3.30	2 x 6.50



1977-79 First commercial lithium-ion battery



TiS₂ cathode

- High capacity of 240 mAh/g
- High cycle durability
- Low voltage of 2V vs. Li/Li⁺
- Requiring a lithium source in anode
- Release of toxic H₂S in contact with moisture

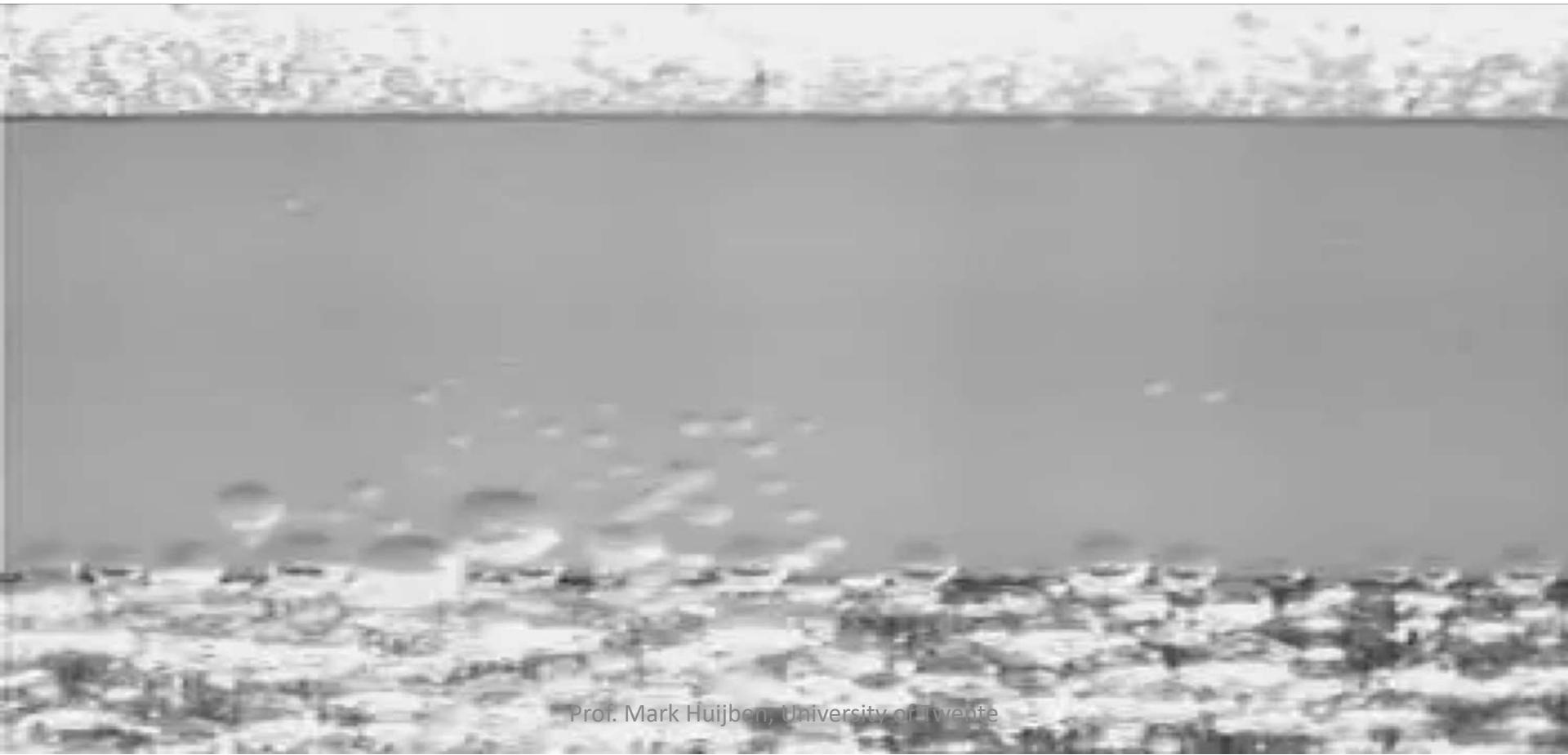
LiClO₄ in liquid electrolyte

Low stability and shock sensitive

Li metal anode

Formation of dendrites during plating

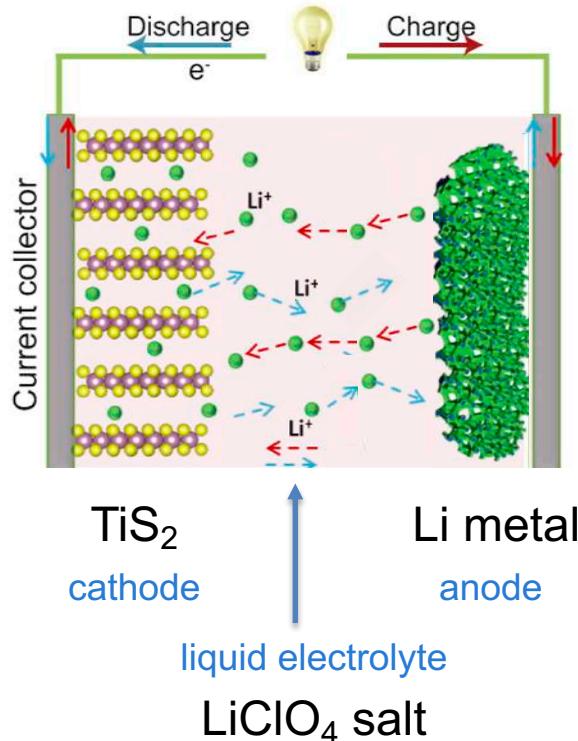
dendrite formation: shorts between electrodes





Prof. Mark Huijben, University of Twente

1977-79 First commercial lithium-ion battery



TiS₂ cathode

- High capacity of 240 mAh/g
- High cycle durability
- Low voltage of 2V vs. Li/Li⁺
- Requiring a lithium source in anode
- Release of toxic H₂S in contact with moisture

LiClO₄ in liquid electrolyte

Low stability and shock sensitive

→ Replaced by (CH₃)₄B

Li metal anode

Formation of dendrites during plating

→ Replaced by LiAl metal

Low cyclability

1977

Solid State Chemistry
of Energy Conversion and Storage

John B. Goodenough, EDITOR

University of Oxford

M. Stanley Whittingham, EDITOR

EXXON Research and Engineering Co.

A symposium sponsored
by the Division of Inorganic
Chemistry at the 171st Meeting
of the American Chemical Society,
New York, N.Y.,
April 5-8, 1976.

ADVANCES IN CHEMISTRY SERIES

163

AMERICAN CHEMICAL SOCIETY
WASHINGTON, D. C. 1977

Goodenough and Whittingham: Solid State Chemistry of Energy Conversion and Storage
Advances in Chemistry; American Chemical Society: Washington, DC, 1977.

John B. Goodenough



Since 1952 : Research scientist
at MIT Lincoln Laboratory

Ferrimagnetic ceramics for random access memory (RAM)

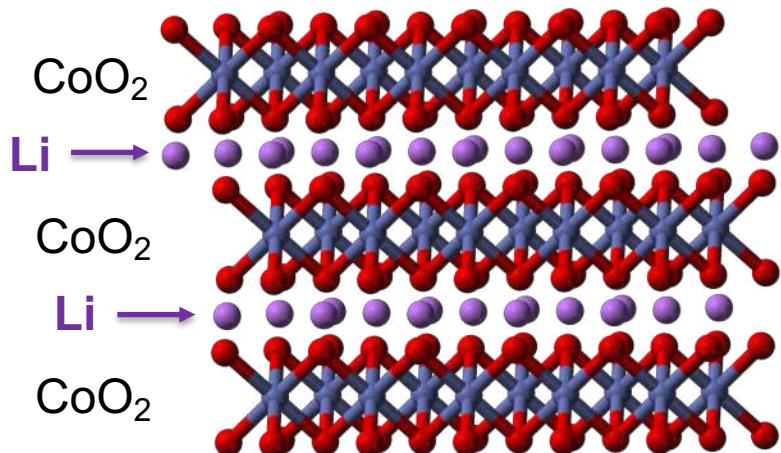
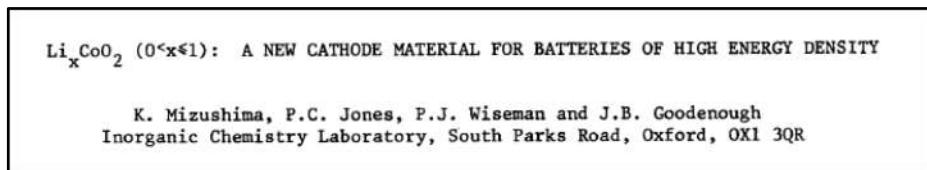
Goodenough-Kanamori rules : to interpret magnetism in solids

Since 1976 : Professor at University of Oxford

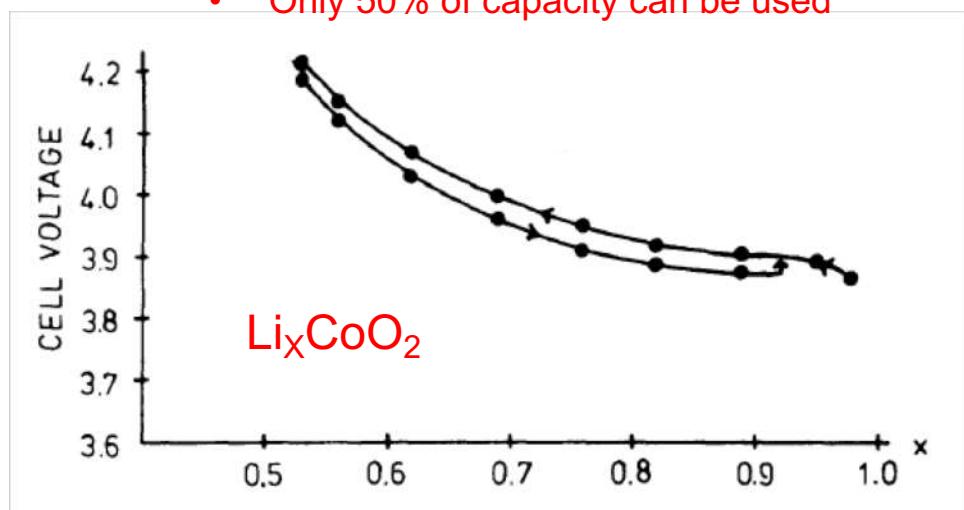
Study oxide ceramics for electrochemistry



1980 Discovery of lithium intercalation into LiCoO_2



- High capacity of 272 mAh/g
- High cycle durability
- High voltage of 4V vs. Li/Li⁺
- No lithium source required in anode
- Sensitive to moisture
- Only 50% of capacity can be used

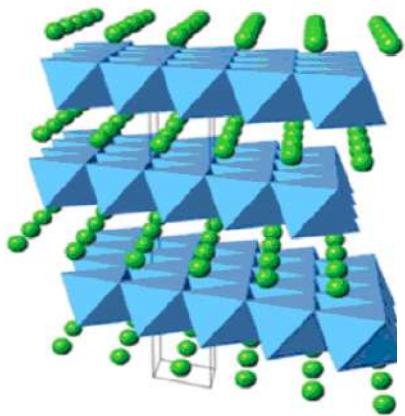


MRS bulletin 15, 783 (1980)

Prof. Mark Huijben, University of Twente

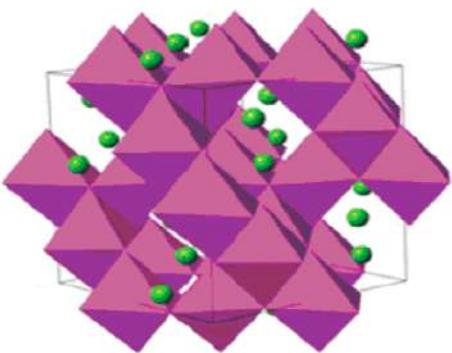
1980-1983 Discovery of various high voltage cathode materials

Layered LiCoO_2
2D

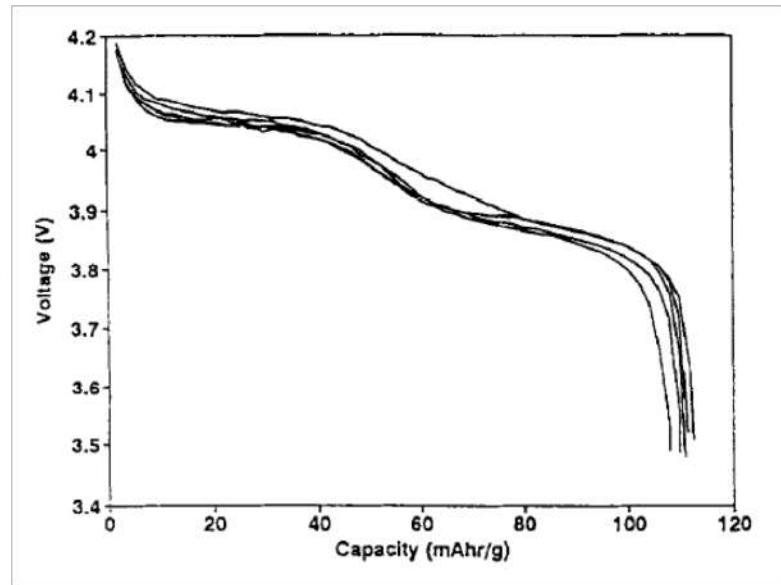


1980

Spinel LiMn_2O_4
3D



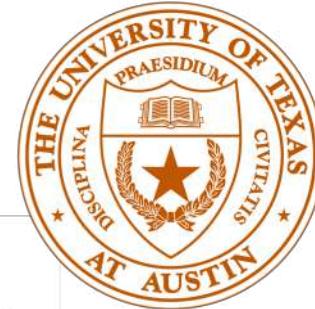
1983



M. M. Thackeray, W. I. F. David, P. G. Bruce, J. B. Goodenough,
MRS bulletin 18, 461 (1983)

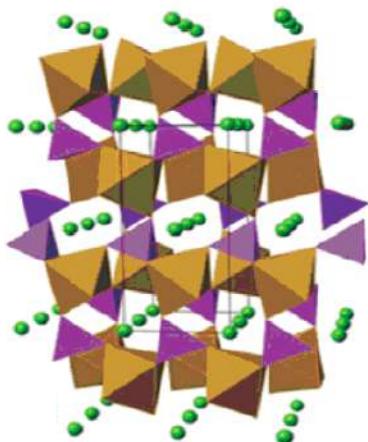
Prof. Mark Huijben, University of Twente

1986 Mandatory retirement in United Kingdom

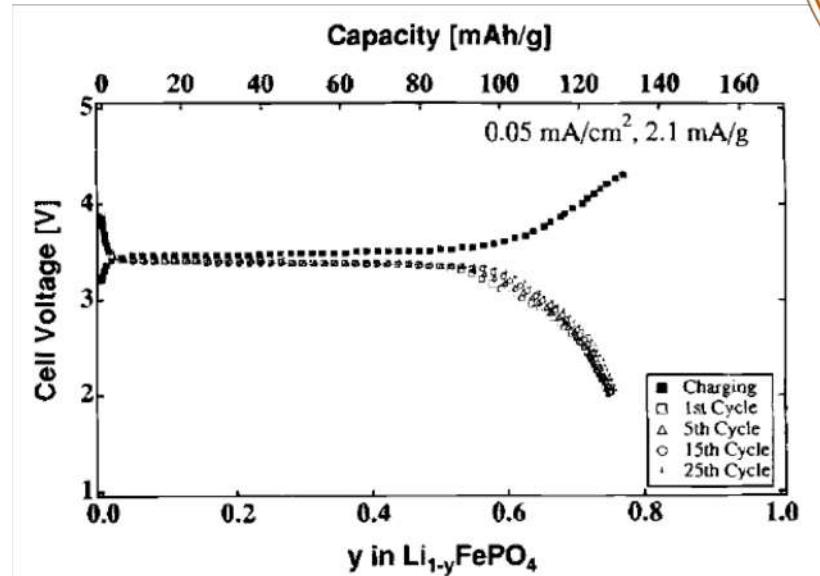


→ University of Texas at Austin

Olivine LiFePO_4
1D

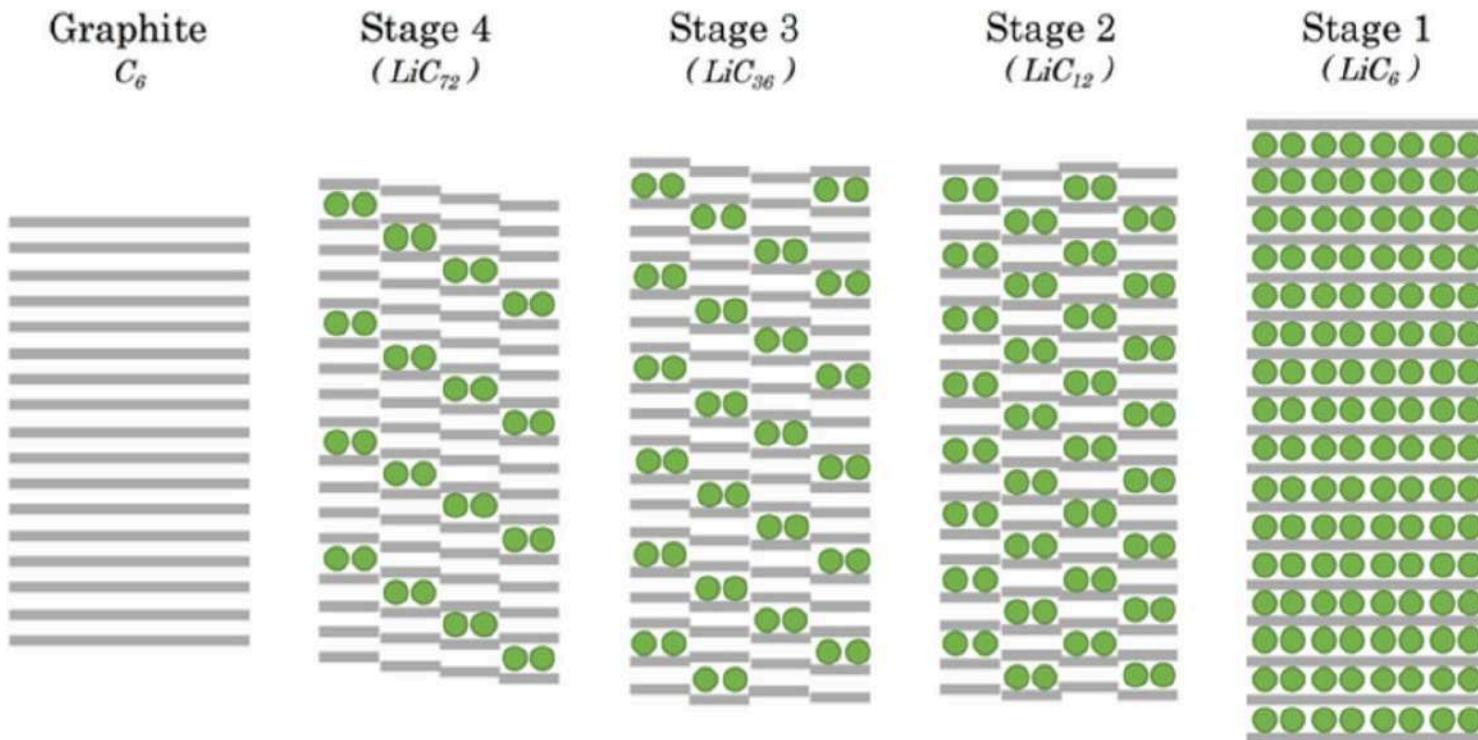


1997



A. K. Padhi, K. S. Nanjundaswami, J. B. Goodenough,
J. Electrochem. Soc. 144, 1188–1194 (1997).
Prof. Mark Huijben, University of Twente

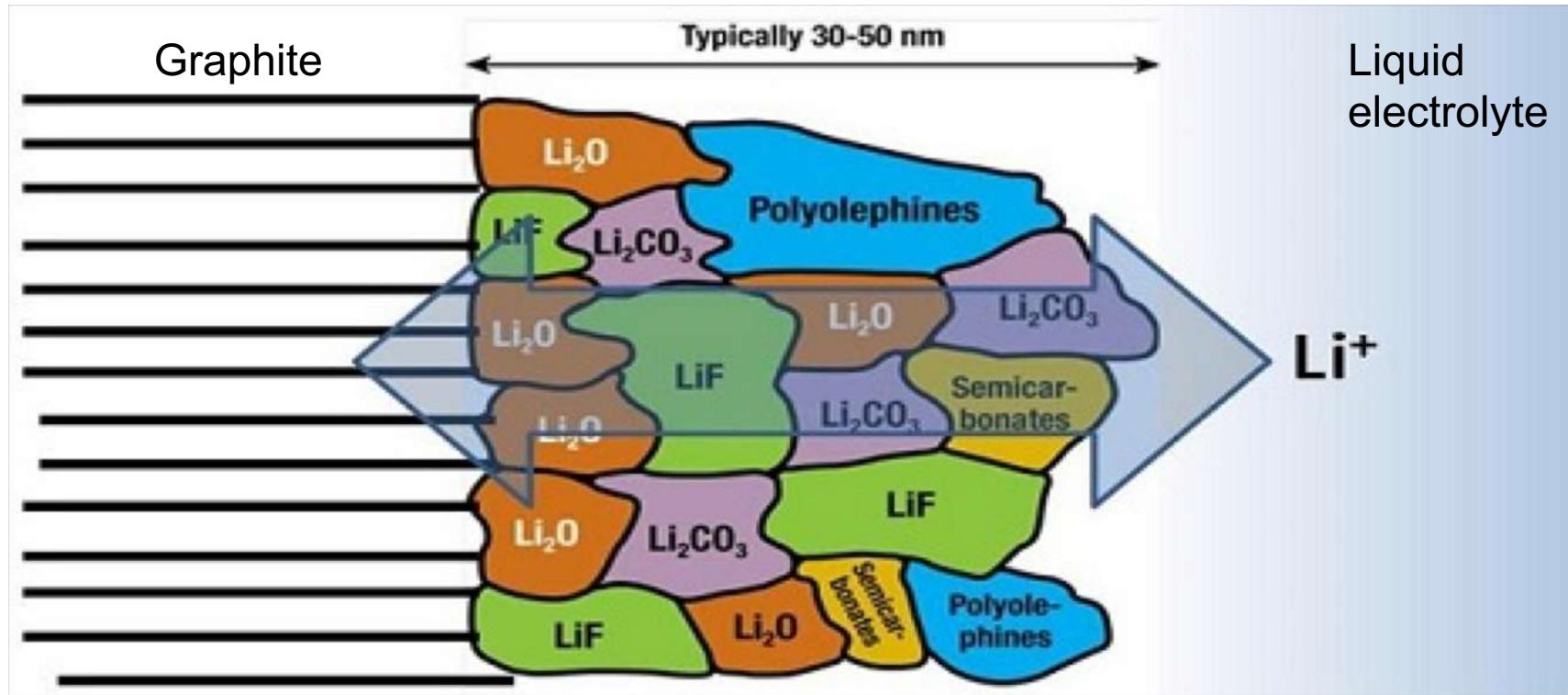
1974 Lithium intercalation into graphite as anode



J. O. Besenhard, H. P. Fritz, J. Electroanal. Chem. 53, 329 (1974).

Prof. Mark Huijben, University of Twente

1979 SEI formation : solid-electrolyte interface

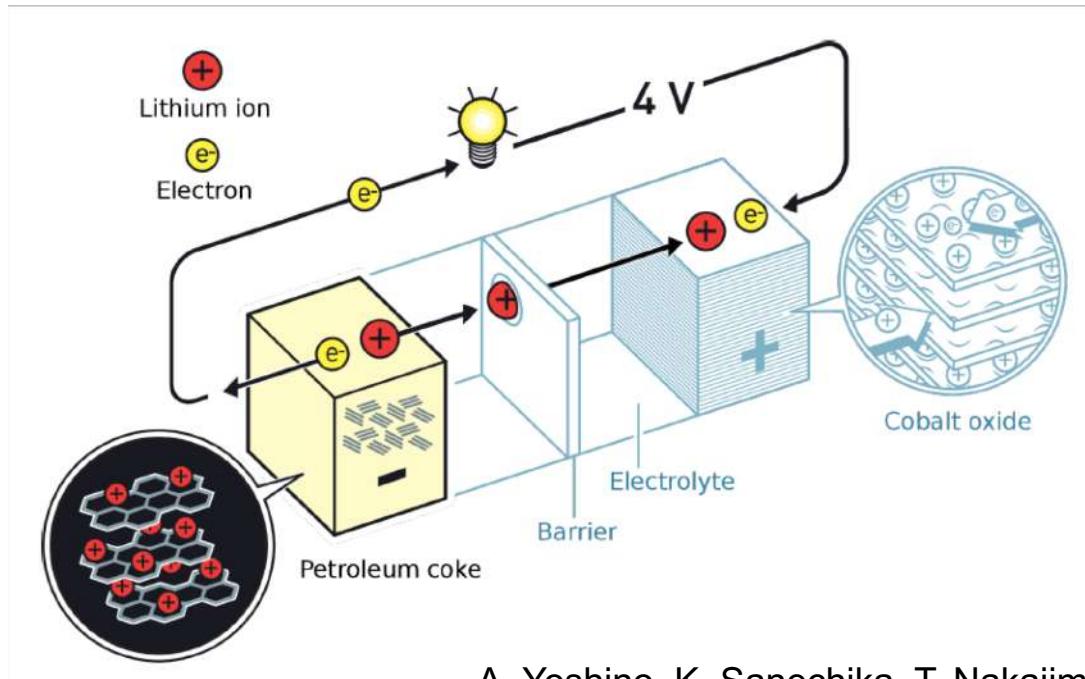


E. Peled, J. Electrochem. Soc. 126, 2047 (1979).
Prof. Mark Huijben, University of Twente

1985 Discovery of soft coke-carbon to substitute graphite

Akira Yoshino, Asahi Kasei Corporation

AsahiKASEI



A. Yoshino, K. Sanechika, T. Nakajima, Japanese patent 1989293 (1985)
US Patent 4668595 A (1987)

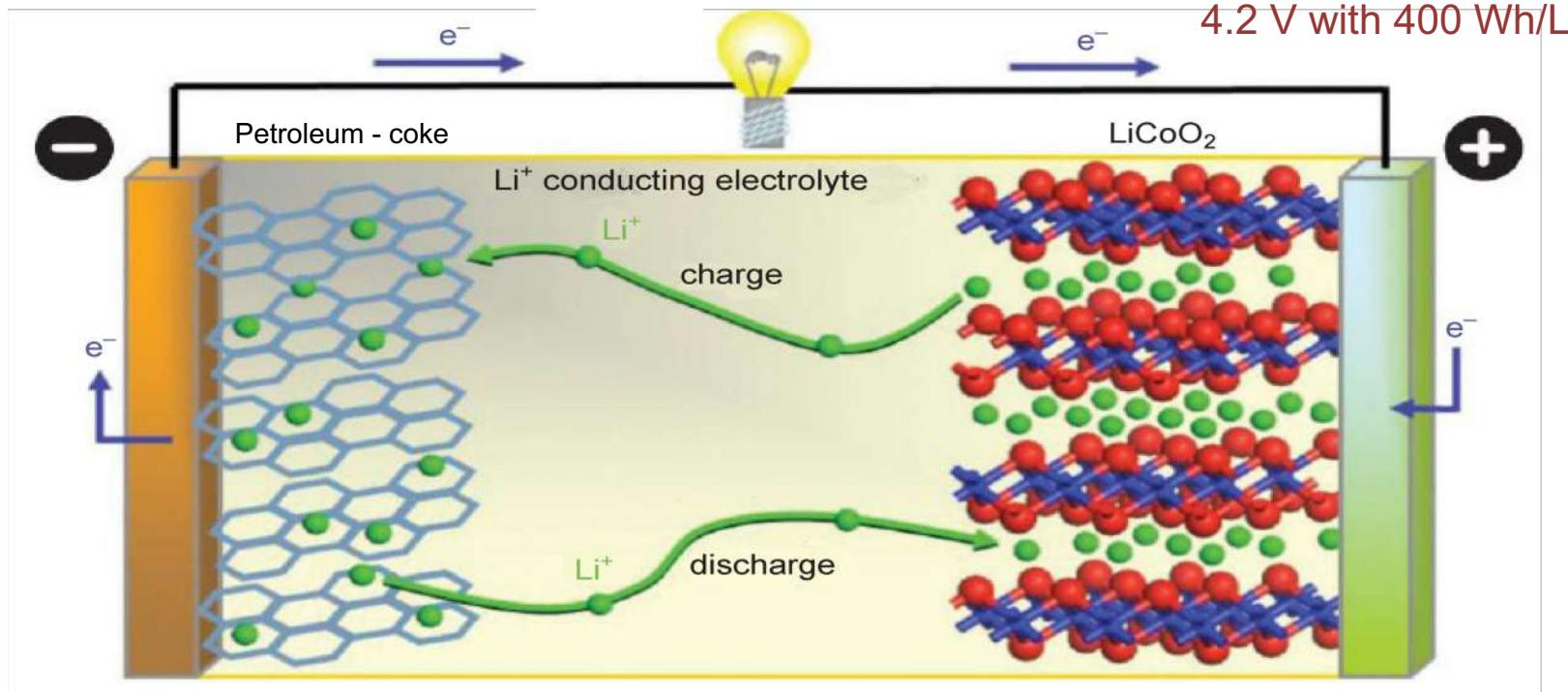
Prof. Mark Huijben, University of Twente

1991 Introduction of first commercial high voltage lithium-ion battery

SONY

4.1 V with 200 Wh/L

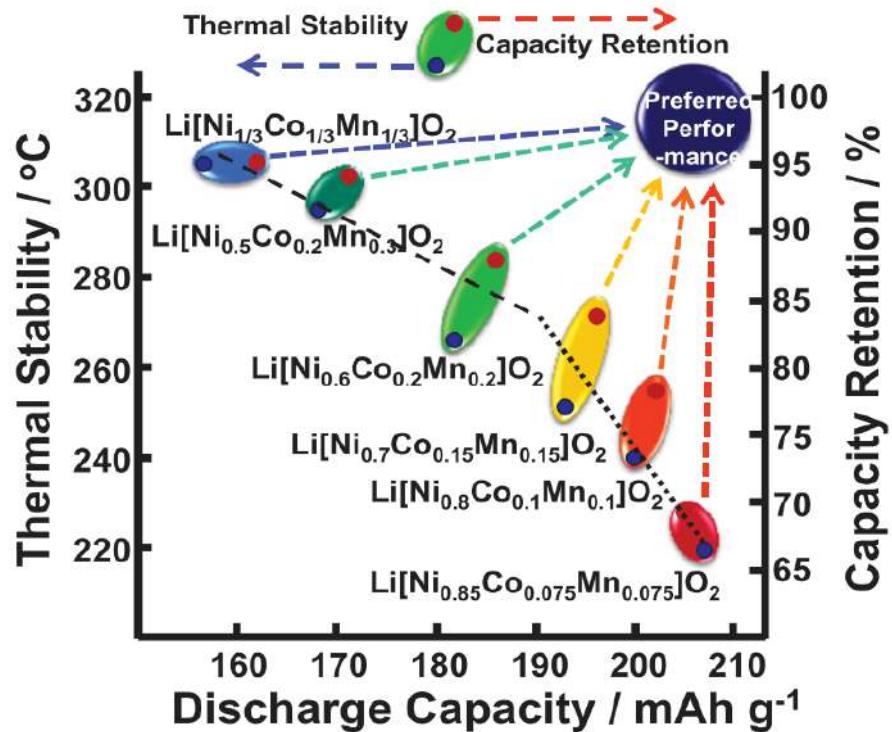
4.2 V with 400 Wh/L



Layered LiCoO_2 and NMC as cathode material



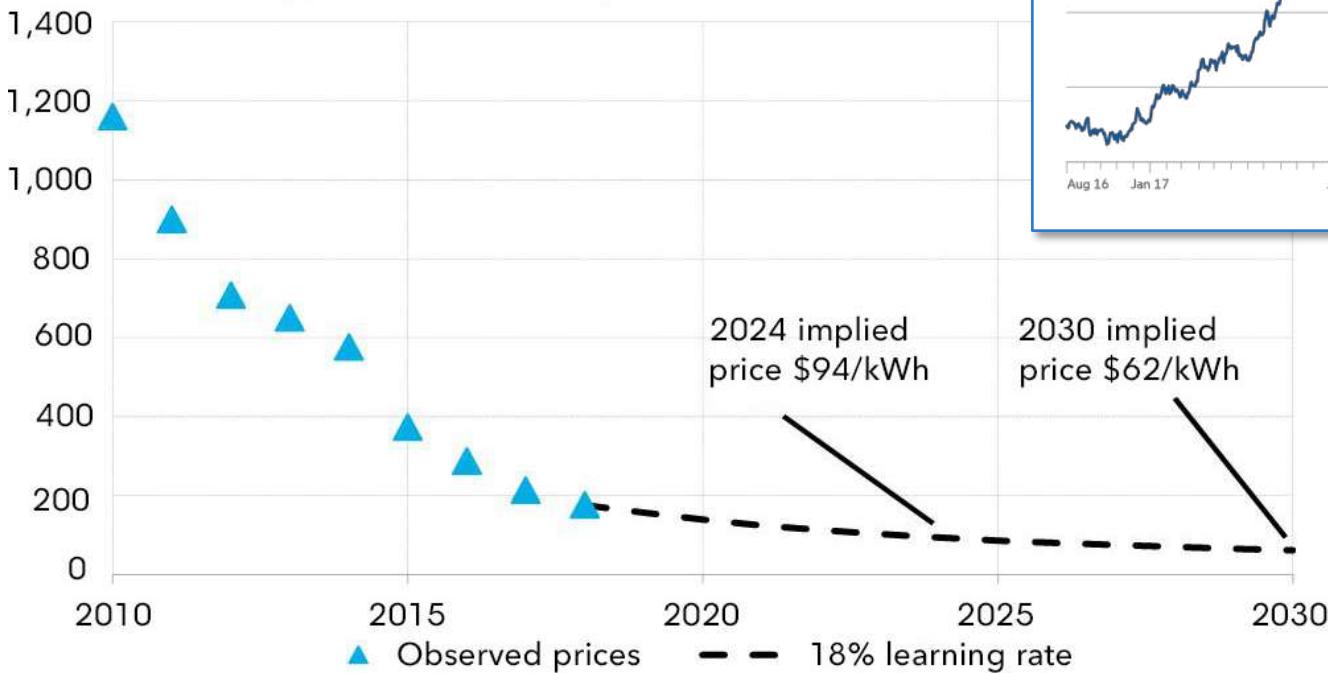
Layered LiCoO_2 and NMC as cathode material



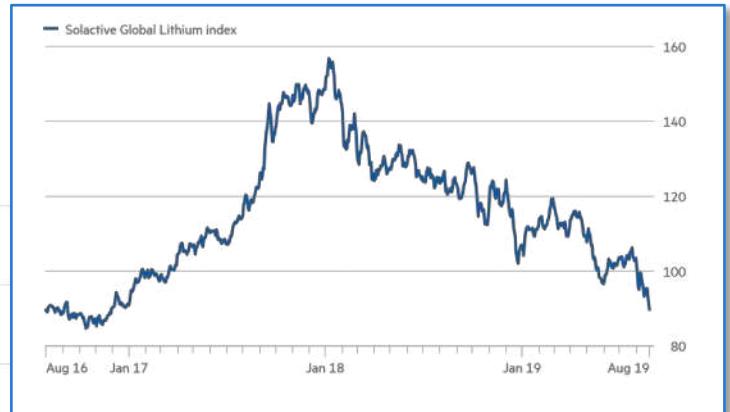
	Energy	Power	Safety	Life	Cost	
LCO lithium cobalt LiCoO_2	+++	+++	+	++	+	
NCA lithium nickel aluminum cobalt $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$	+++	++	-	++	-	
LMO lithium manganese LiMn_2O_4	-	+++	++	-	++	
NMC lithium nickel manganese cobalt $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$	++	++	++	+++	+++	
LFP lithium iron phosphate LiFePO_4	+	+++	+++	++	++	

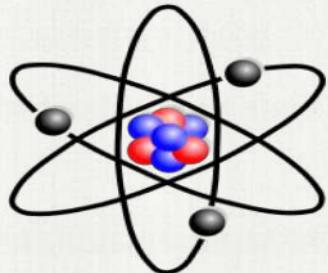
Lithium-ion battery price

Lithium-ion battery pack price (real 2018 \$/kWh)



Source: BloombergNEF





PRINTED IN U.S.A.

You Deserve The Original

7up

That's Your Assurance

Why we have the youngest customers in the business

This young man is 11 months old—and he isn't our youngest customer by any means.

For 7-Up is so pure, so wholesome, you can even give it to babies and feel good about it. Look at the back of a 7-Up bottle. Notice that all our ingredients are listed. (That isn't required of soft drinks, you know—but we're proud to do it and we think you're pleased that we do.)

By the way, Mom, when it comes to toddlers—if they like to be coaxed to drink their milk, try this: Add 7-Up to the milk in equal parts, pouring the 7-Up gently into the milk. It's a wholesome combination—and it works! Make 7-Up your family drink. You like it . . . it likes you!

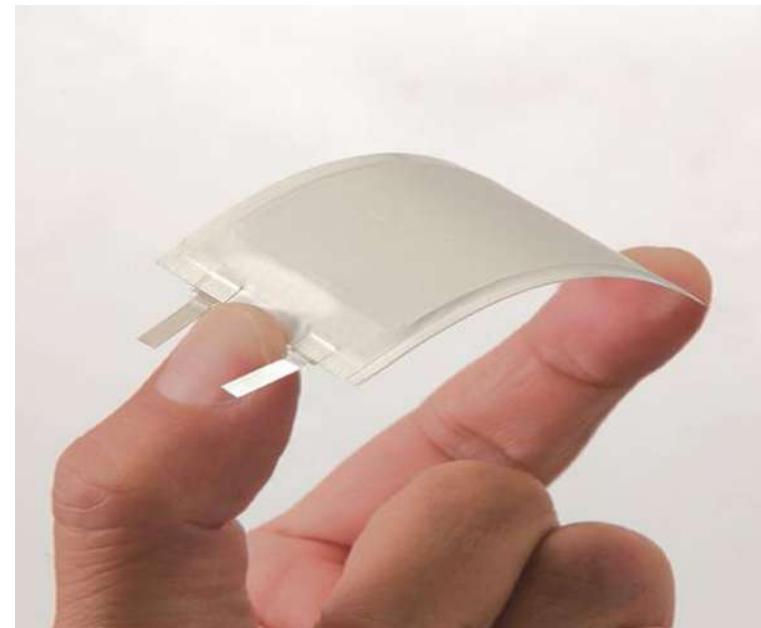
Nothing does it like Seven-Up!

Prof. Mark Huijben, University of Twente

Conventional battery



Solid-state battery



1 HIGH SPECIFIC ENERGY



2 HIGH SPECIFIC POWER



3 AFFORDABLE COST



4 LONG LIFE



5 HIGH SAFETY



6 WIDE OPERATING RANGE



7 NO TOXICITY



8 FAST CHARGING



9 LOW SELF-DISCHARGE

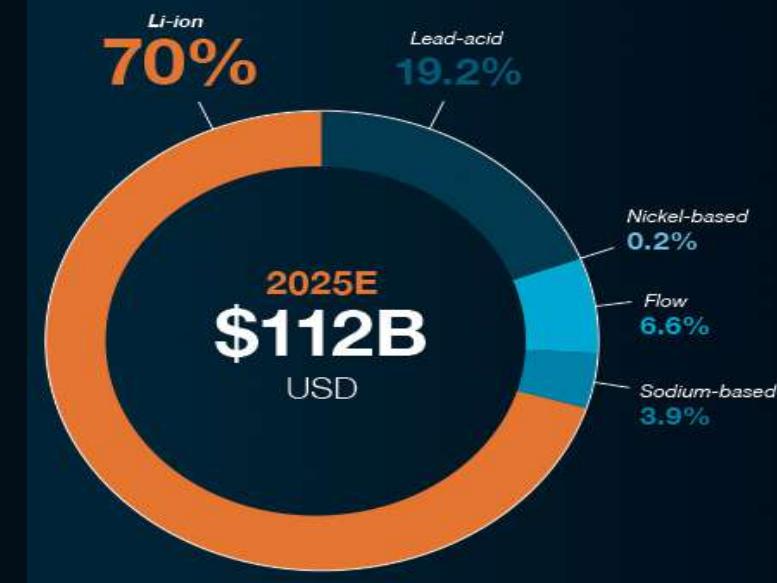


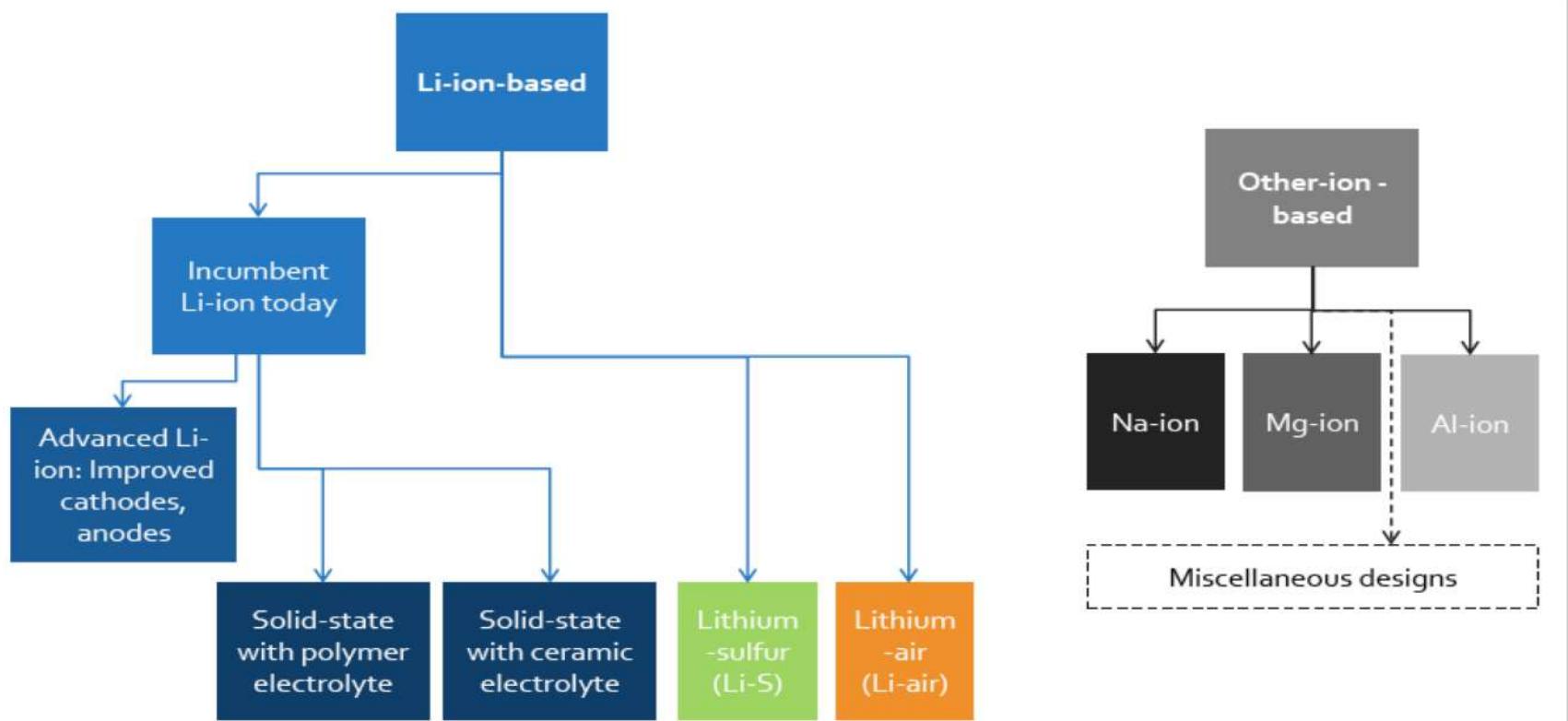
10 LONG SHELF LIFE

10 MAJOR
PROPERTIES

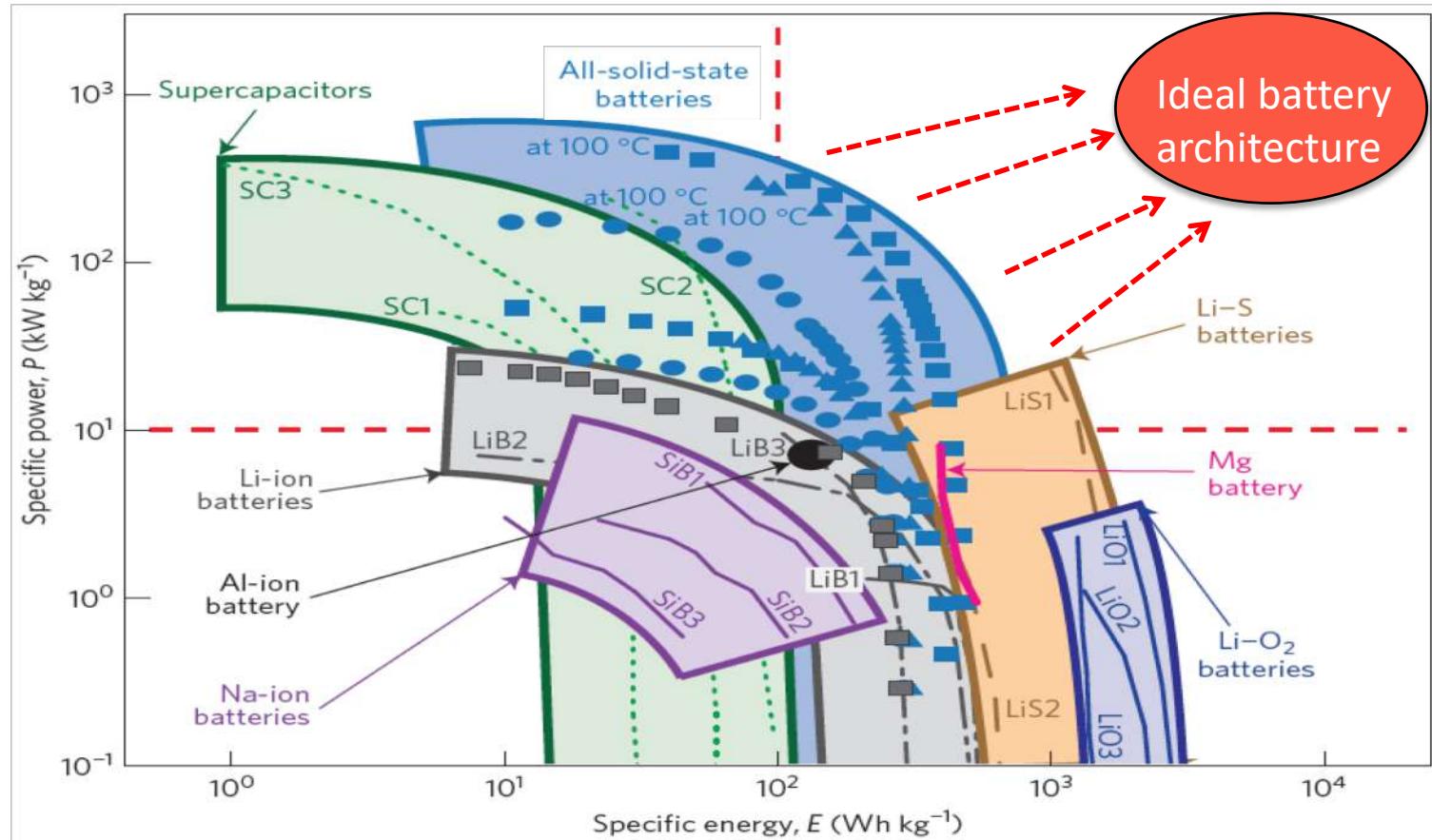
FOR ASSESSING BATTERIES

Rechargeable Battery Market



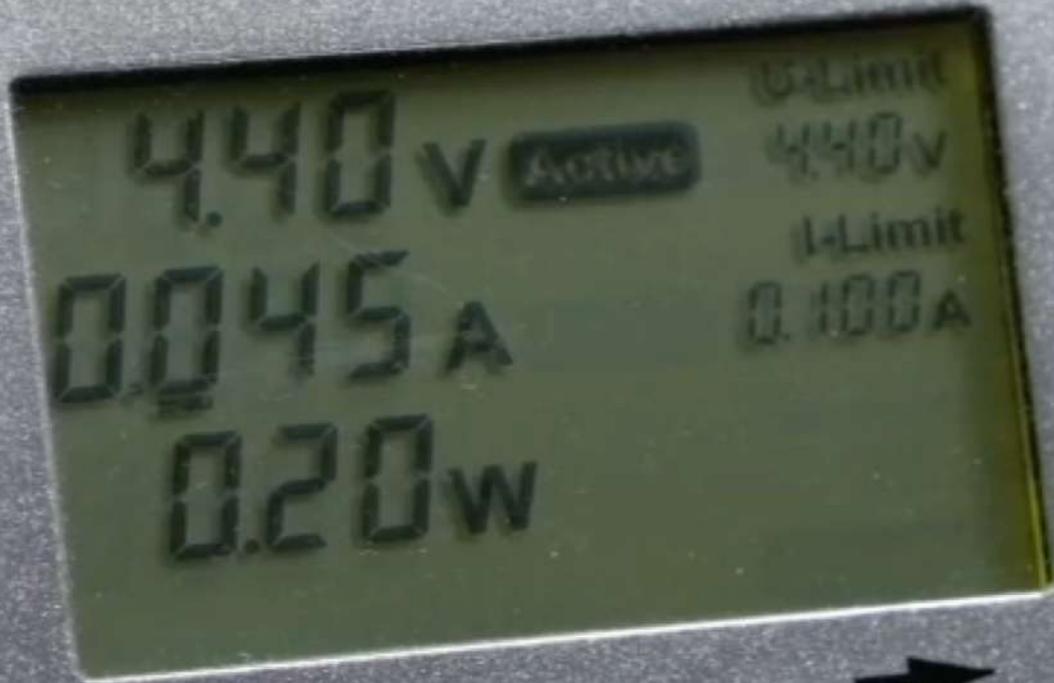


Battery technologies



5315

Master



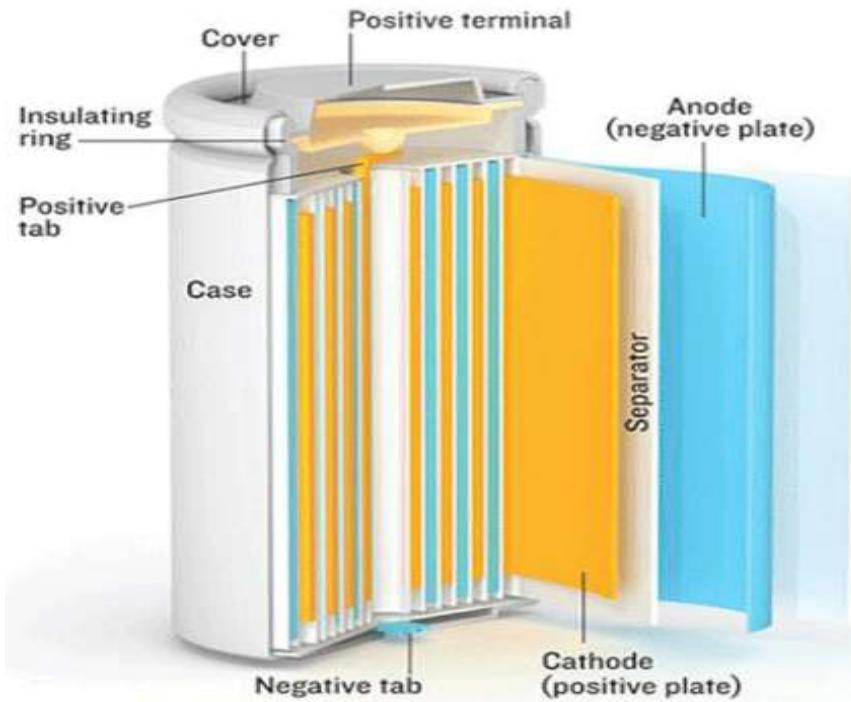
Master
Slave



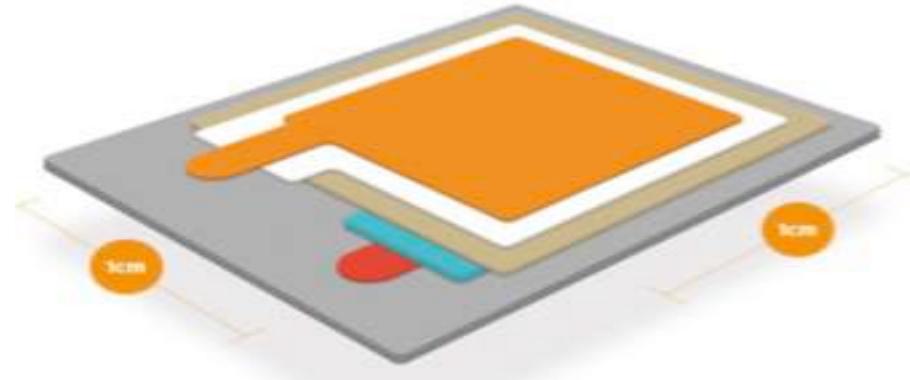
U/I



Conventional battery



Solid-state battery



Orange	Anode Current Collector
White	Anode
Brown	Electrolyte
Cyan	Cathode
Red	Cathode Current Collector
Grey	Substrate

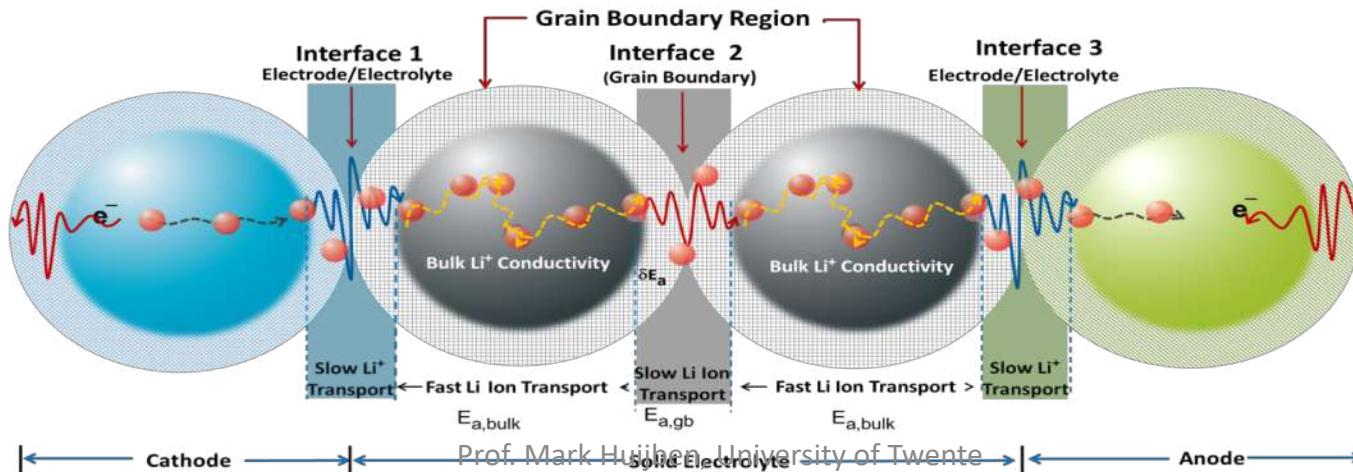


Grand challenge : Mastering control of the interfaces

Aim: Enhanced interfacial conductivities (ionic and electronic)

- Controlled interface formation (stable SEI, no dendrites, etc.)
- Control of lithium-ion flux for (dis)charge rates
- Better strain accommodation during lithium extraction/insertion
- New reactions not available in bulk materials.

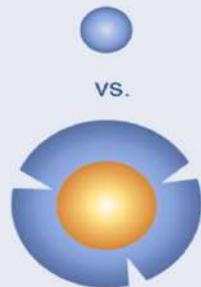
Example: Interfaces in solid-state batteries



Interface Engineering: strategies

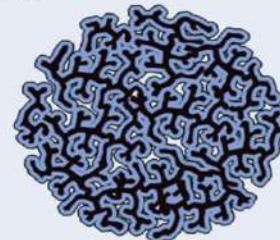
(a) Dimension Reduction

- Faster ion & electron transport
- Higher surface reactivity
- Relief of stress(s) & improved mechanical stability



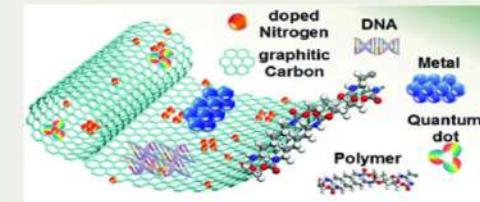
(b) Composite Formation

- Conductive media
- Mechanical (structural) support



(c) Doping & Functionalization

- Faster ion & electron transport
- Improved chemical & thermal stability



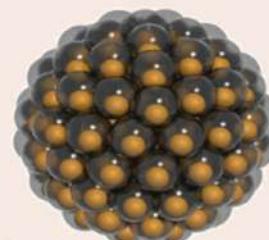
(d) Morphology Control

- Improved structural stability
- Faster ion, electron, & phonon transport
- Modified reactivity



(e) Coating & Encapsulation

- Protection from electrolyte
- Prevention of electrolyte decomposition
- Stabilization of surface reactions
- Conductive media



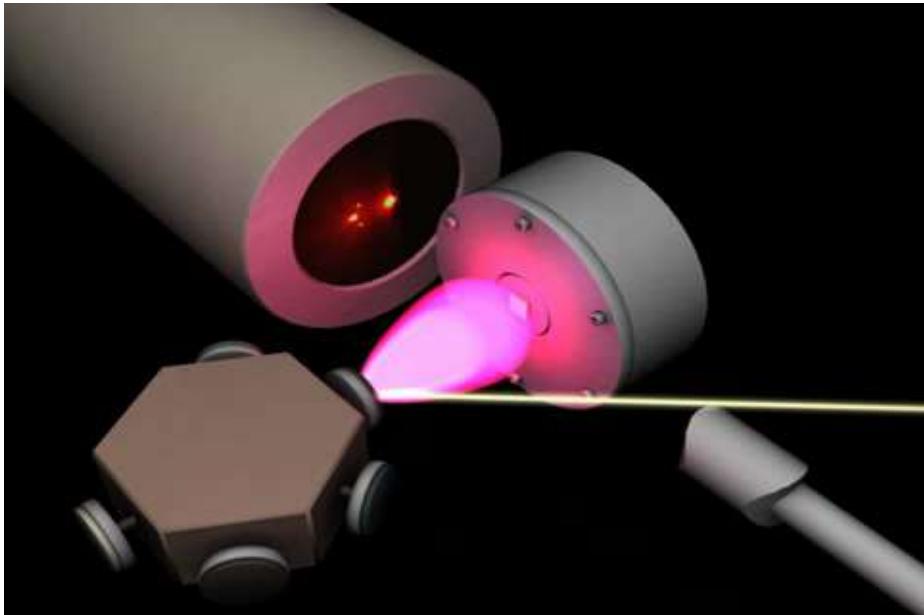
(f) Electrolyte Modification

- Formation of passivation layer(s) on the surface of electrode(s)
- Controlled solubility of active material(s) & decomposition product(s)



Lithium-ion thin film model systems

TWENTE CENTRE FOR
**ADVANCED
BATTERY
TECHNOLOGY**



Studied materials:

Cathode:

LiMn_2O_4 , LiCoO_2 ,
 $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$

Electrolyte:

$\text{Li}_{1/2}\text{La}_{1/2}\text{TiO}_3$, $\text{Al}:\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$

Anode:

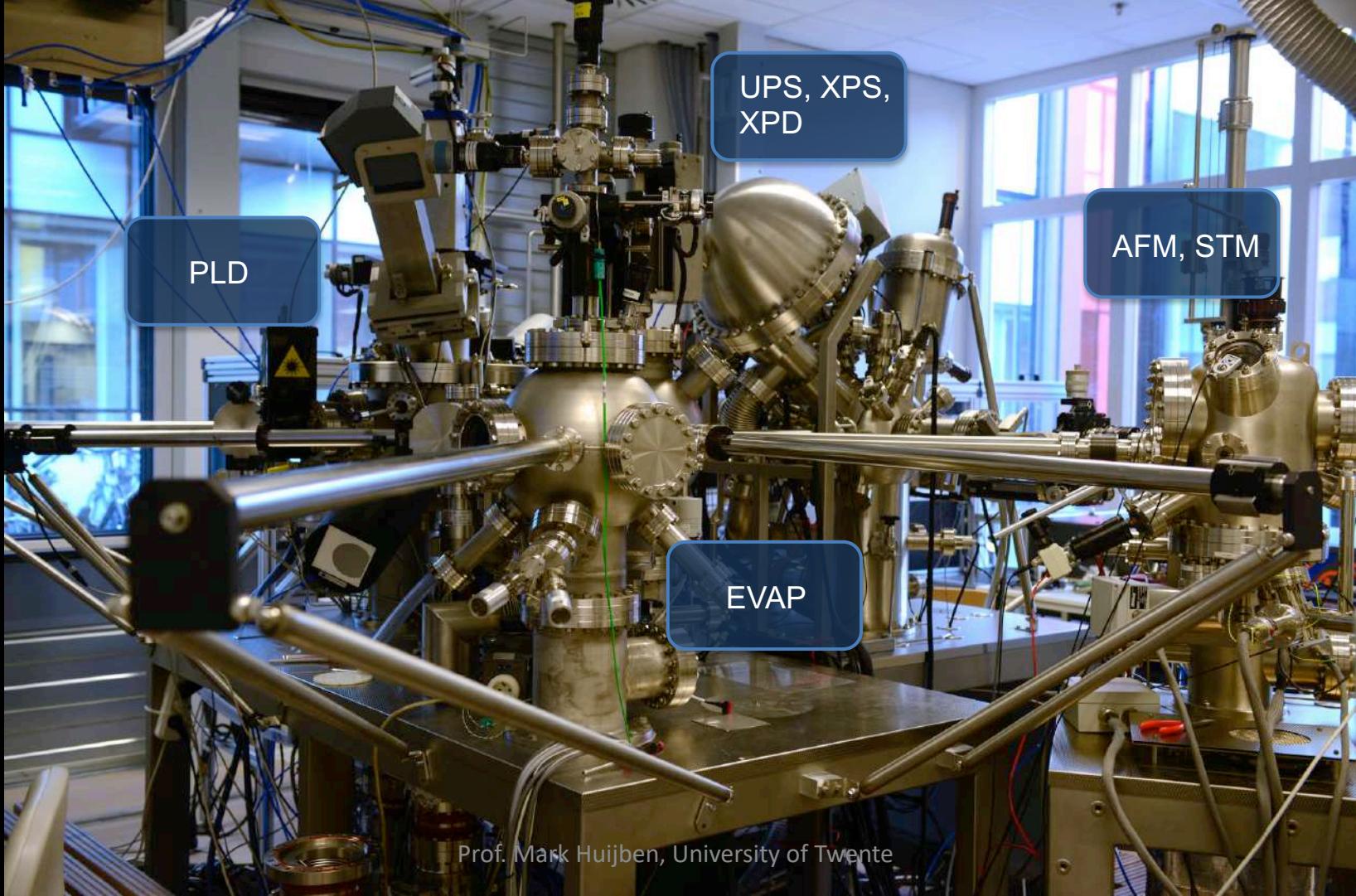
$\text{Li}_4\text{Ti}_5\text{O}_{12}$, $\text{Nb}_{18}\text{W}_{16}\text{O}_{93}$

Composites:

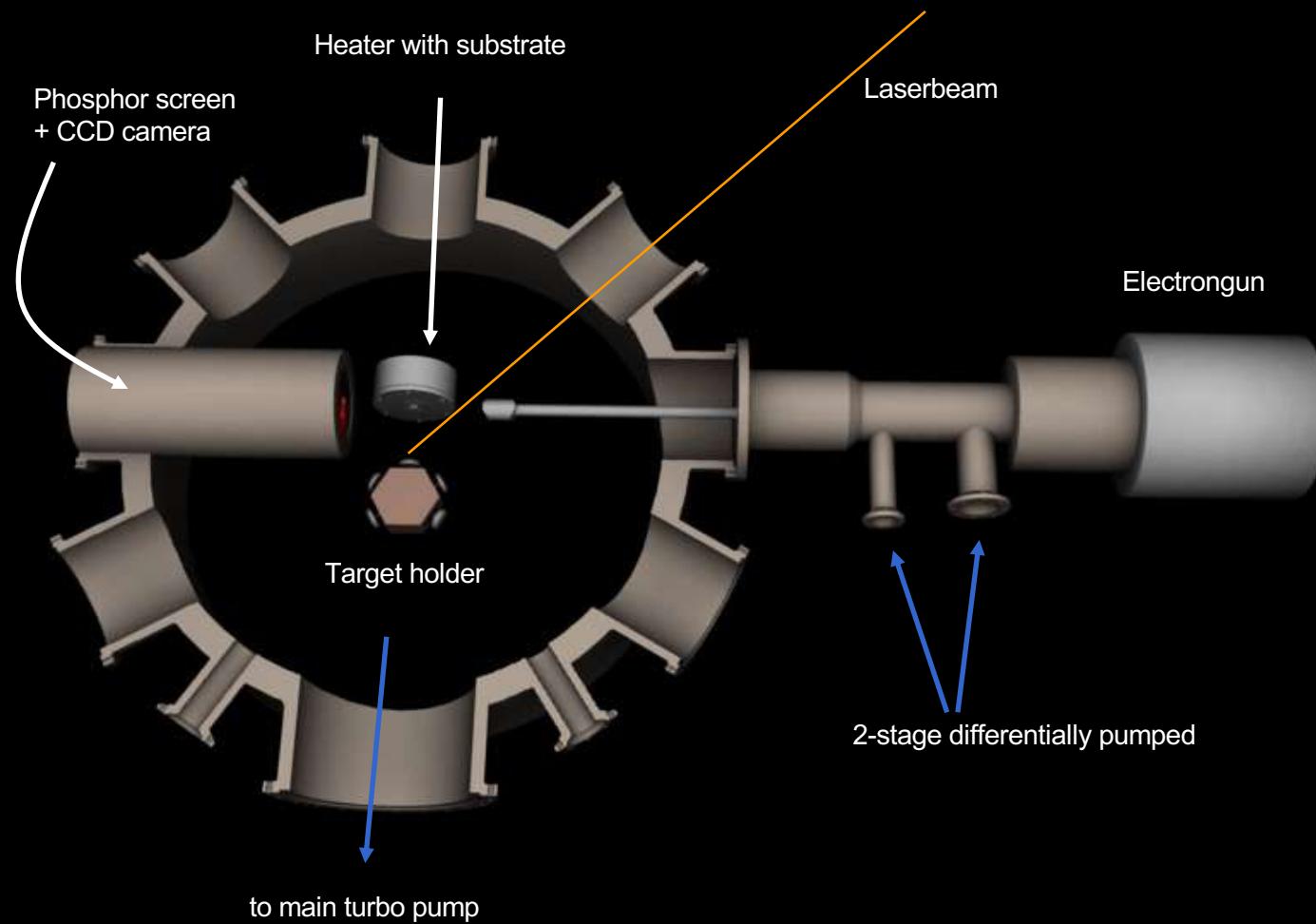
$\text{LiMn}_2\text{O}_4/\text{Li}_{1/2}\text{La}_{1/2}\text{TiO}_3$

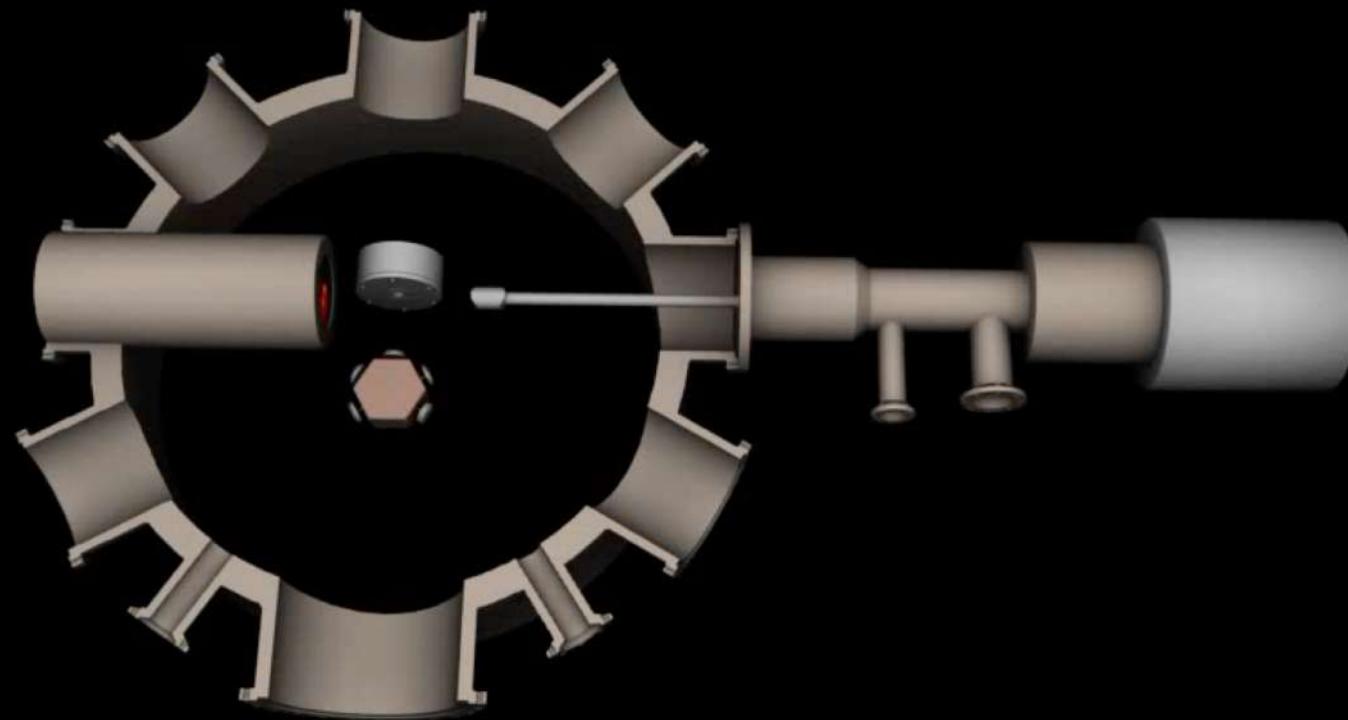
Not through PLD: LiPON (FZ-Jülich, Tokyo)





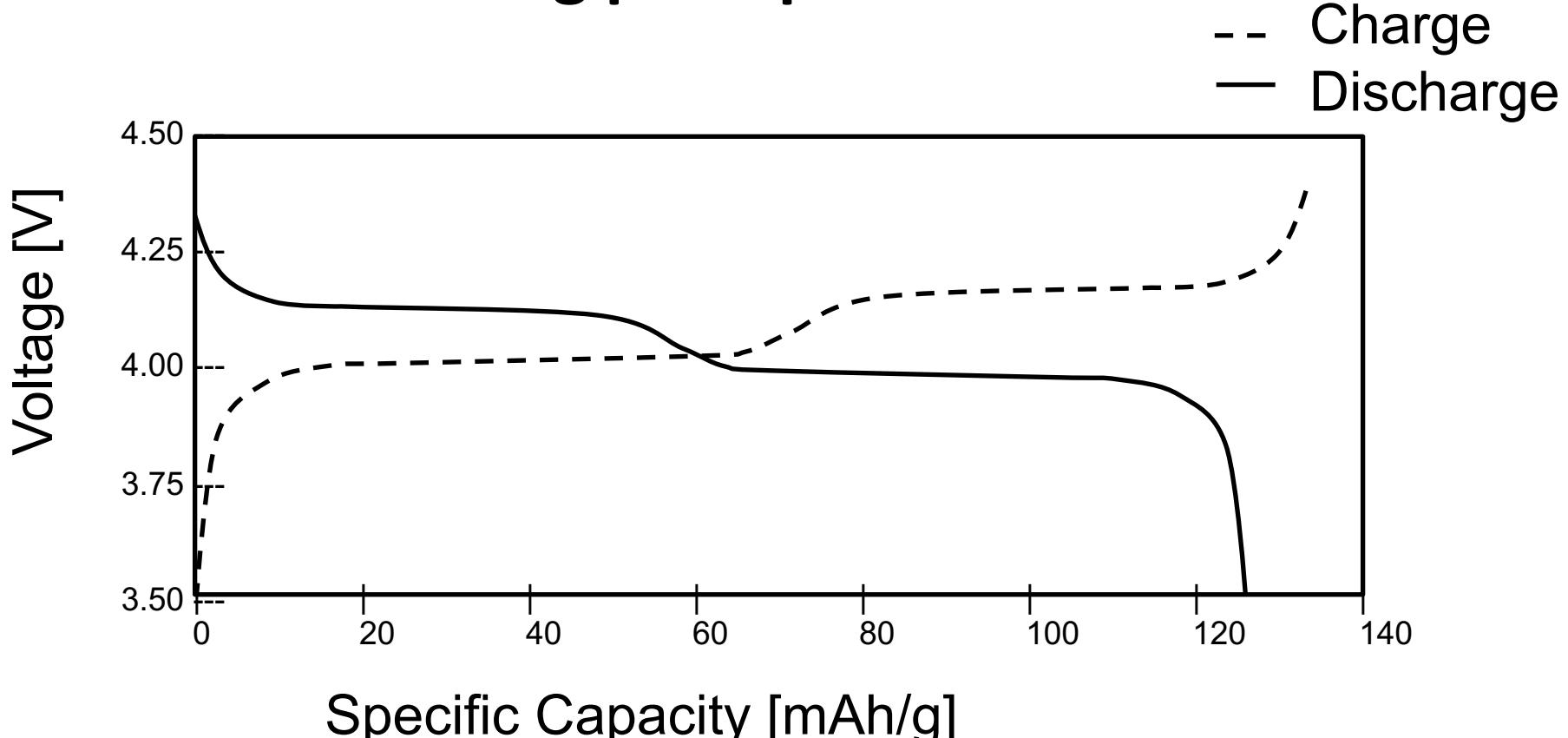
Prof. Mark Huijben, University of Twente



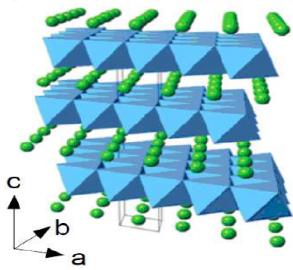


Prof. Mark Huijben, University of Twente

Batteries: working principle



High voltage cathode materials : dimensionality

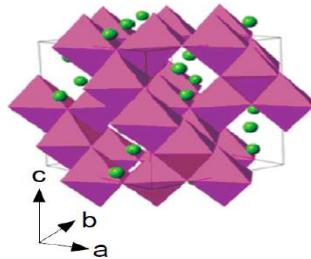


Compound

Specific capacity
(mAh g⁻¹)

Average potential
(V vs. Li⁰/Li⁺)

Energy Density
(Wh kg⁻¹)



LiCoO₂

272 (140)

4.0

1088 (560)

LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂

272 (200)

4.0

1088 (800)

LiMn₂O₄

148 (125)

4.1

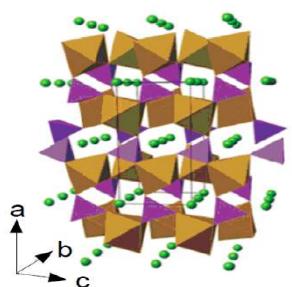
607 (513)

LiMn_{1.5}Ni_{1/2}O₄

148 (125)

4.7

696 (588)



LiFePO₄

170 (160)

3.4

587 (552)

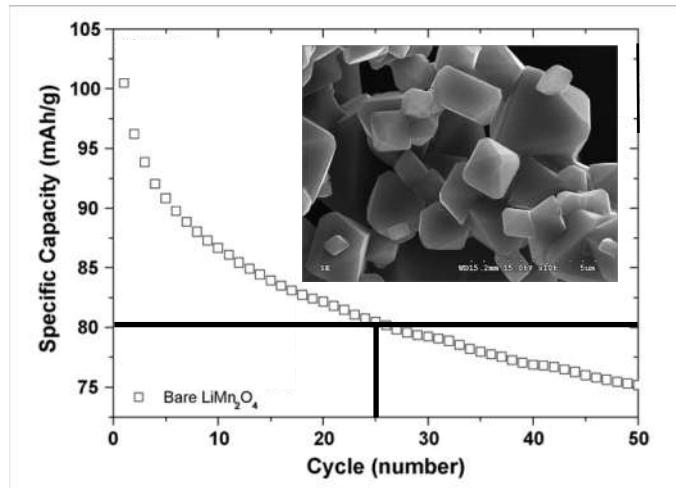
LiFe_{1/2}Mn_{1/2}PO₄

170 (160)

3.4/4.1

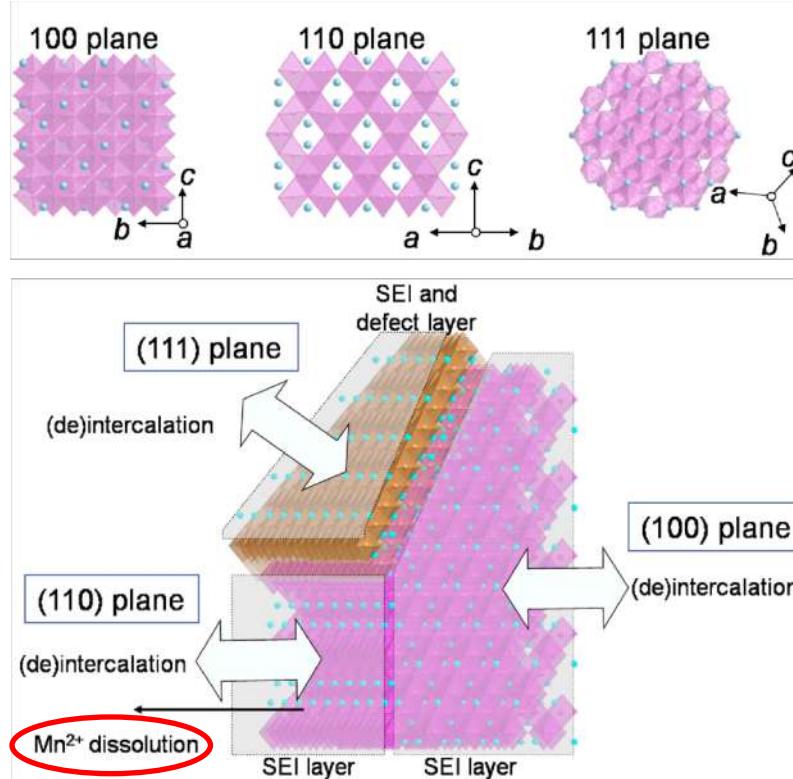
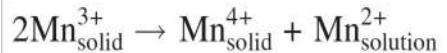
638 (600)

LiMn_2O_4 cathode limitation

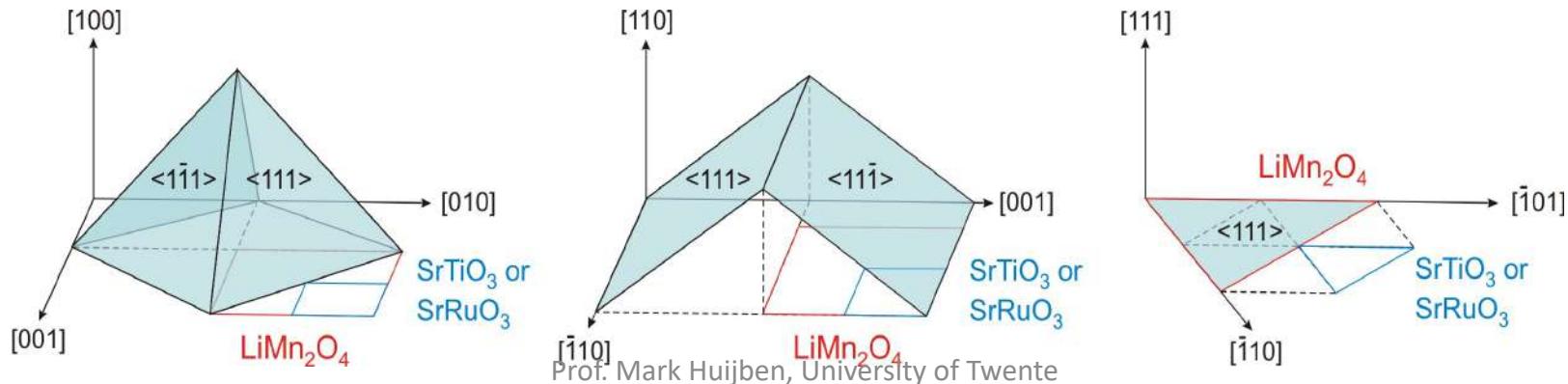
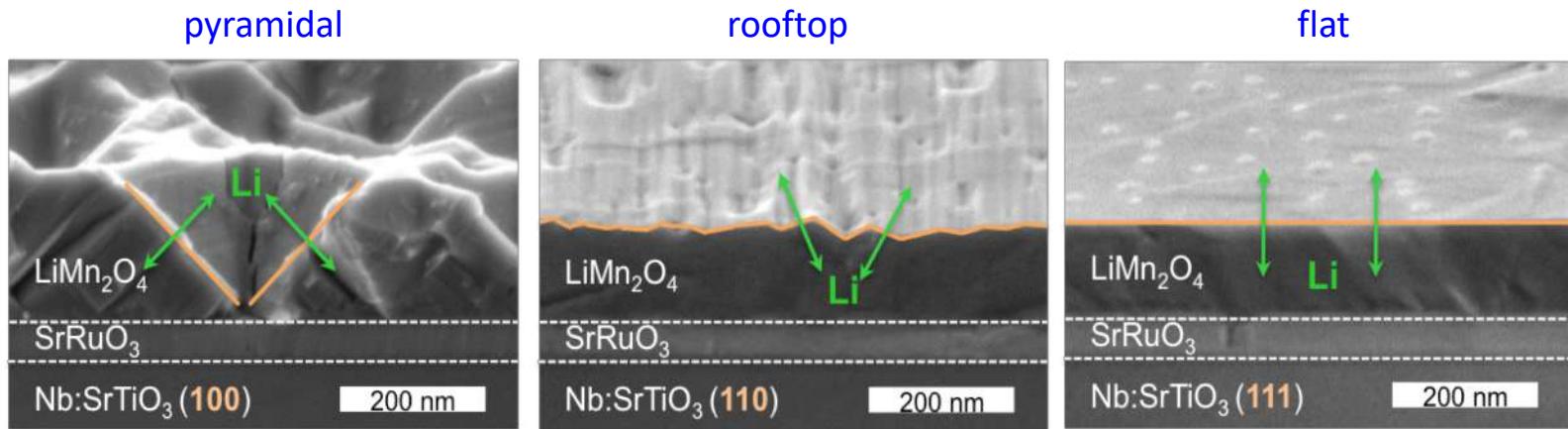


Problem: capacity fade on battery cycling

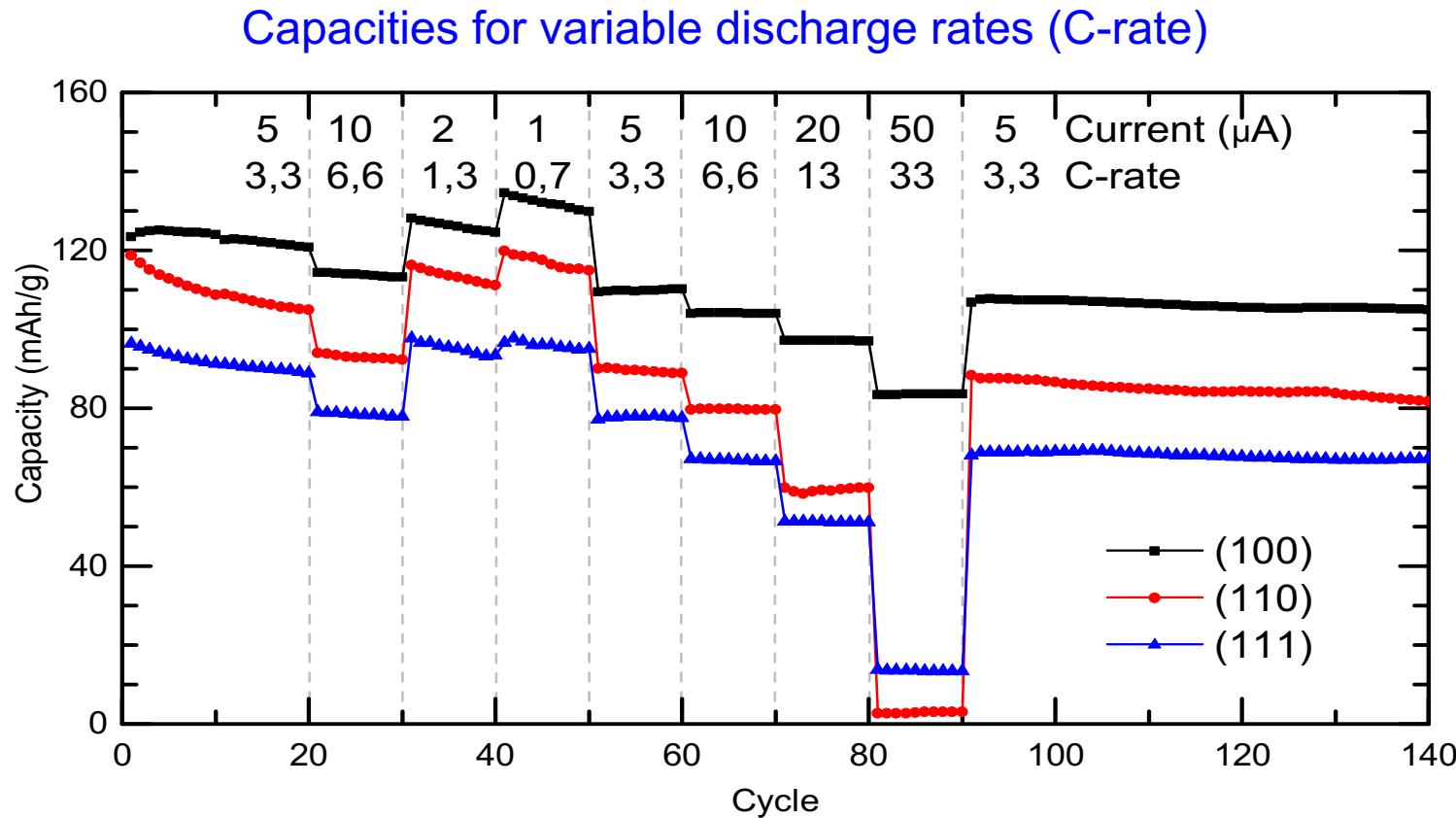
Mn ions dissolved into liquid electrolyte



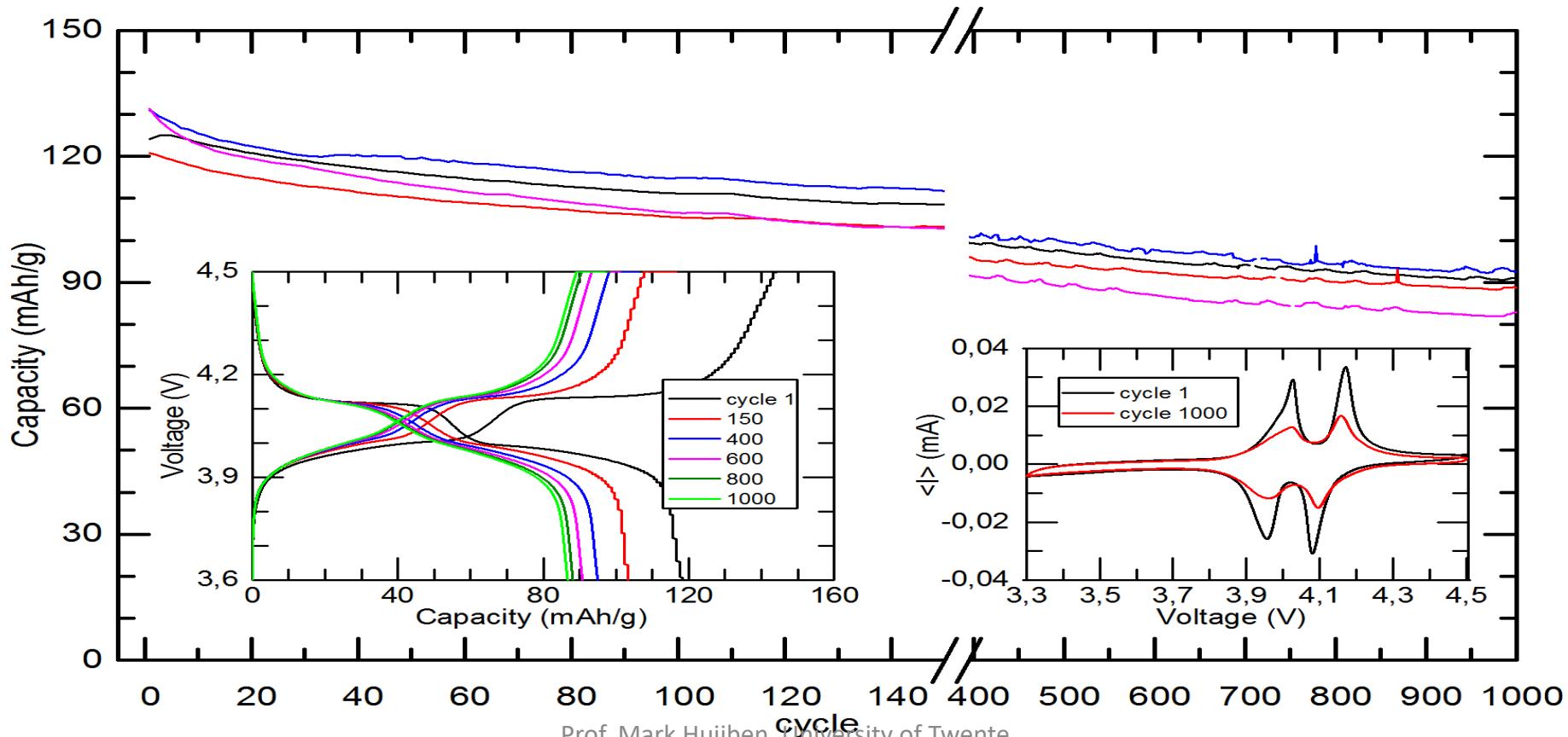
LiMn_2O_4 thin films : controlled model systems



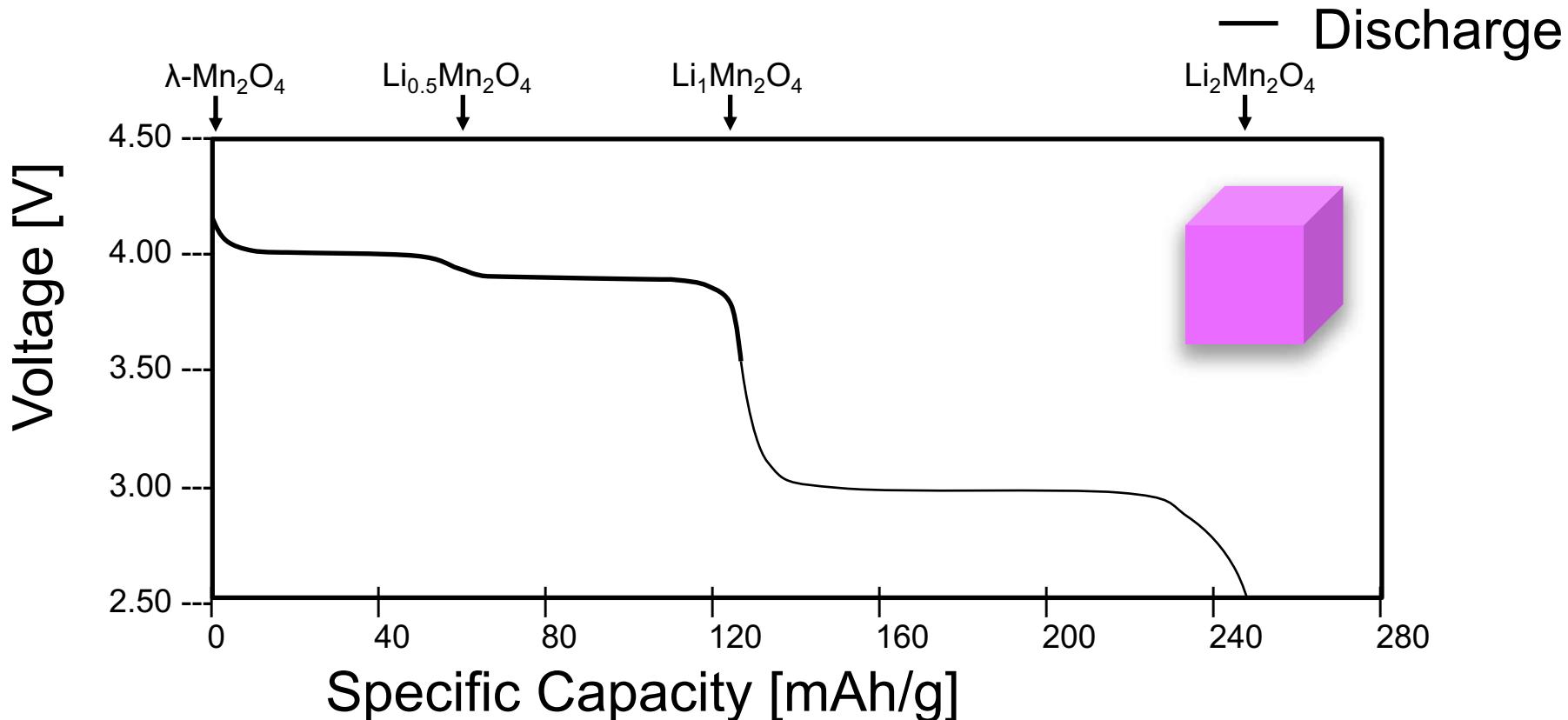
LiMn_2O_4 thin films : lithium kinetics



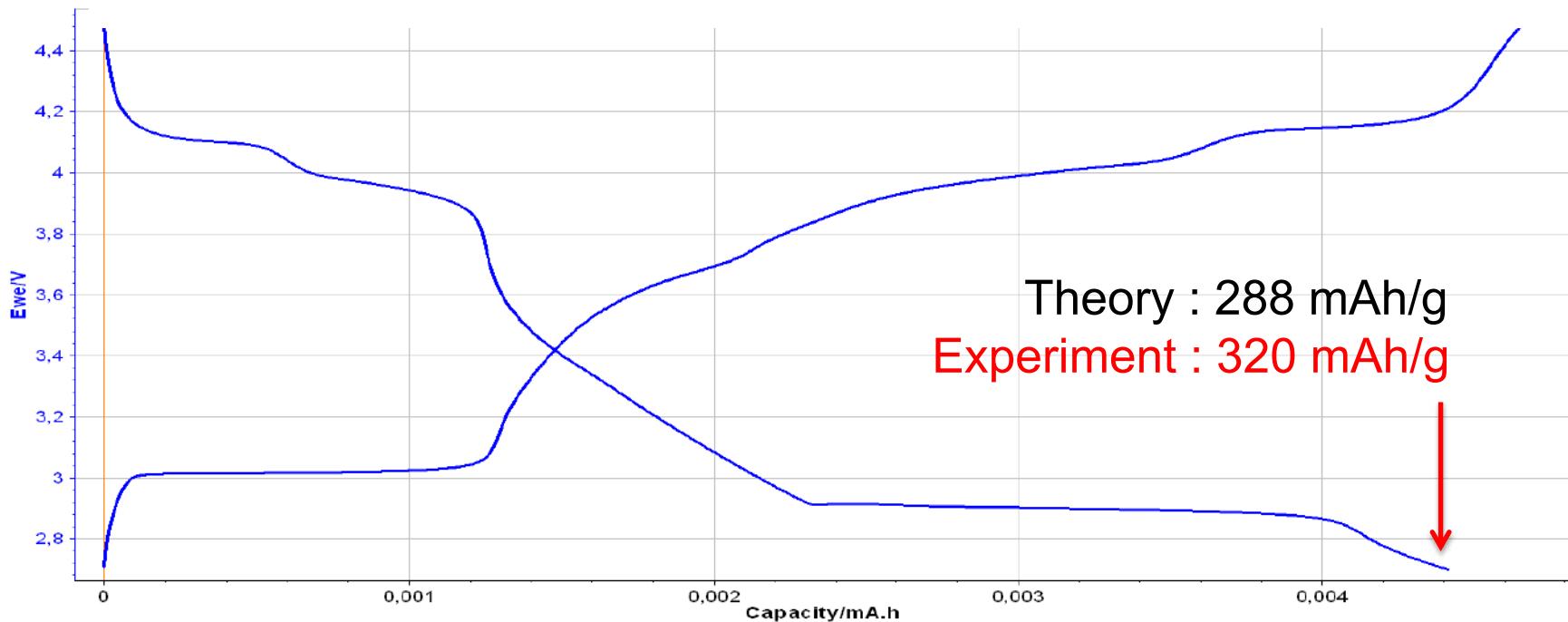
LiMn_2O_4 thin films : cyclability



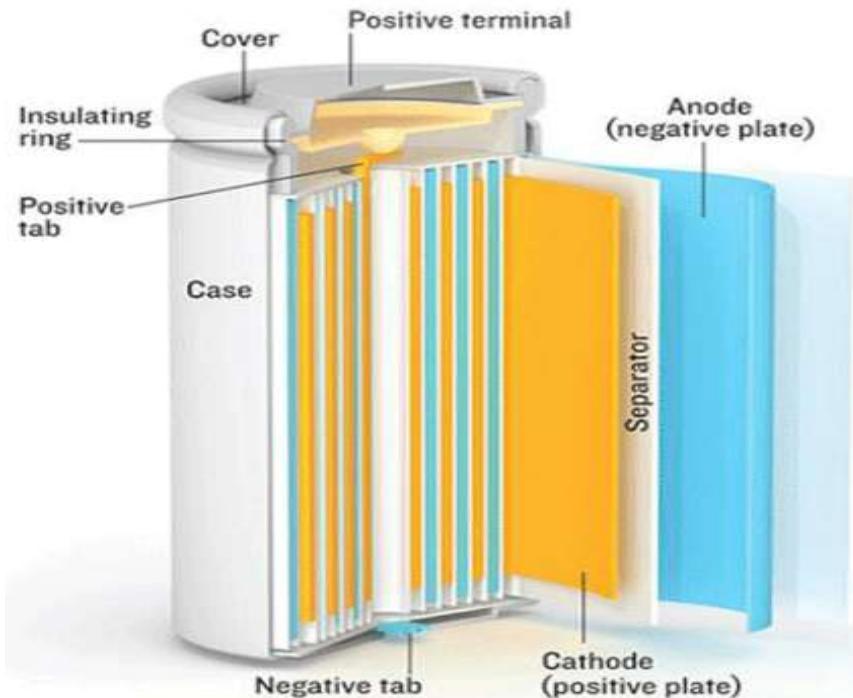
LiMn_2O_4 cathodes: doubling capacities



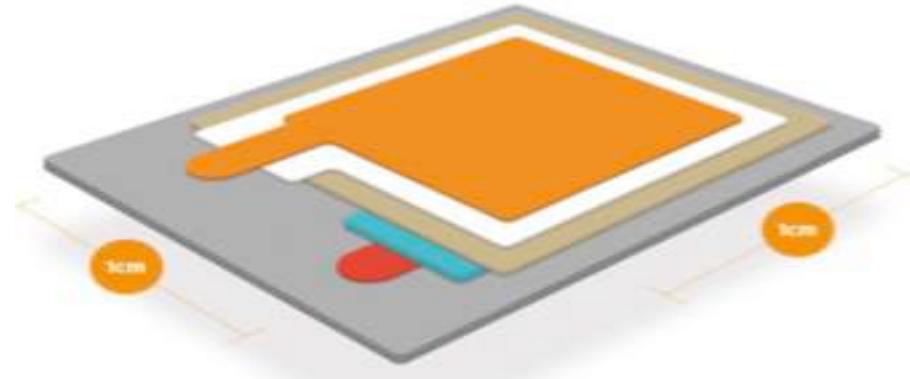
LiMn_2O_4 cathodes: doubling capacities



Conventional battery

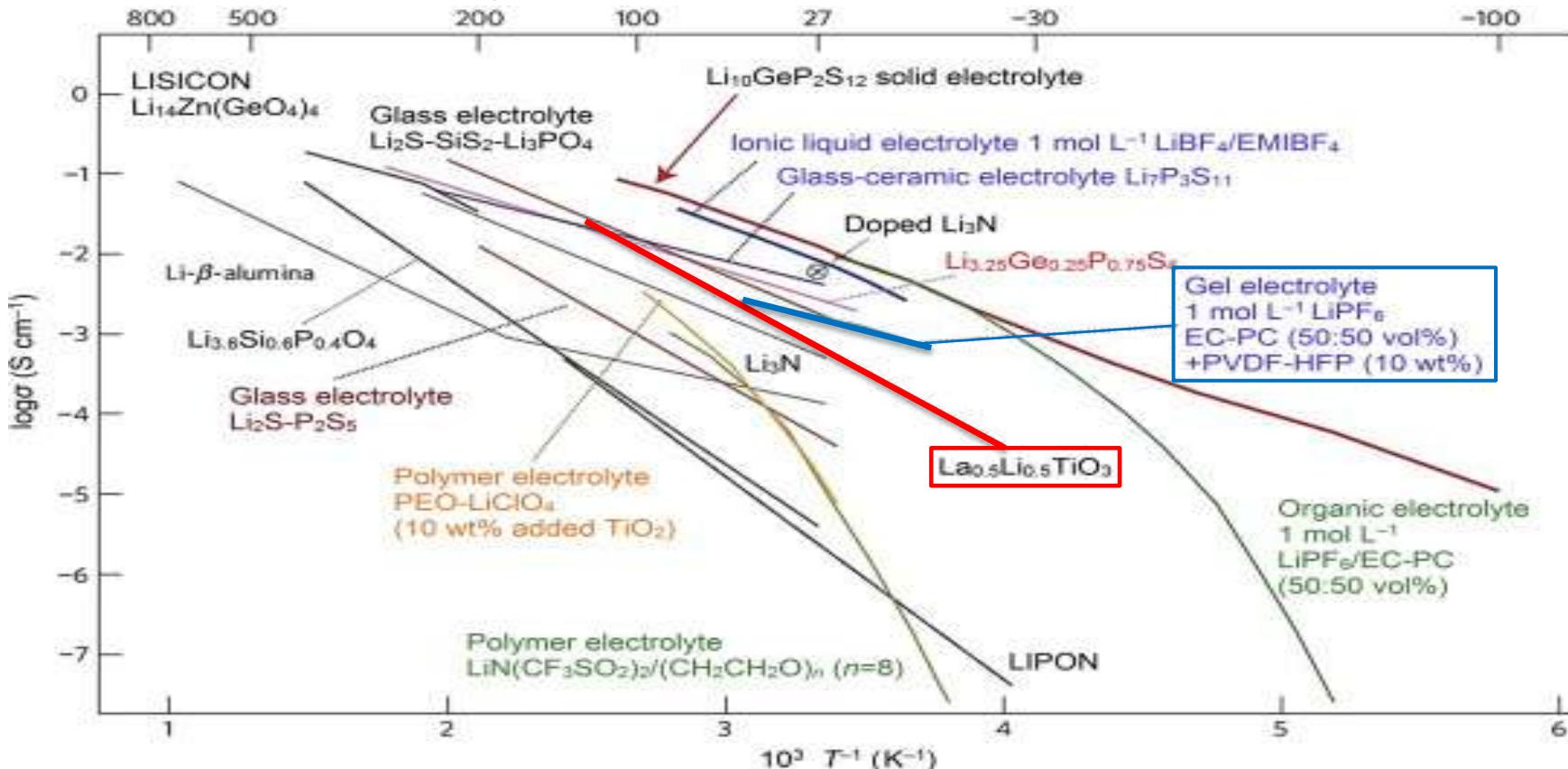


Solid-state battery

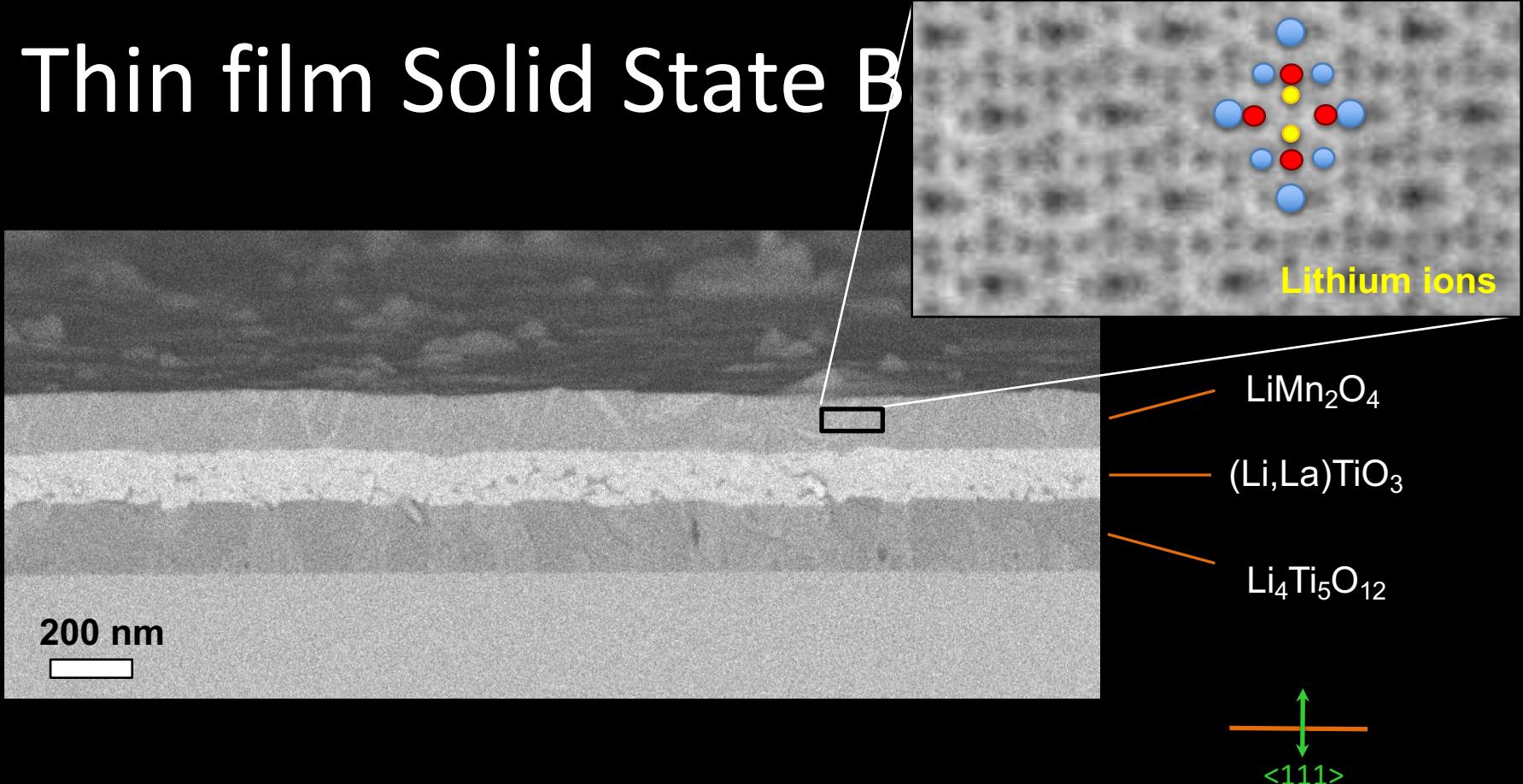


	Anode Current Collector
	Anode
	Electrolyte
	Cathode
	Cathode Current Collector
	Substrate

Solid-state electrolytes



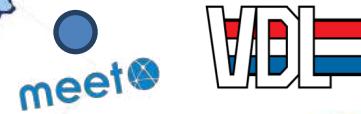
Thin film Solid State B



National Science Agenda (NWA)

Knowledge partners

- 5 universities
- 5 universities of applied sciences



Twente Centre for Advanced Battery Technology

www.utwente.nl/tcabt

Advanced Materials
& Electrochemistry

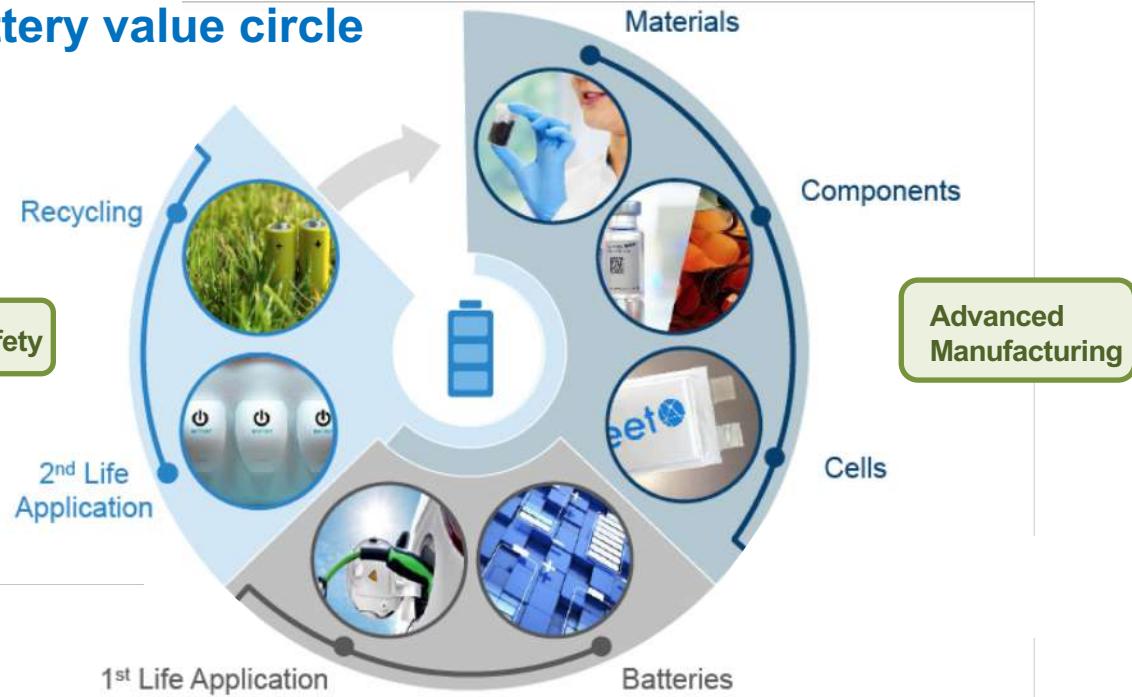
Battery value circle

MESA+
INSTITUTE

DIGITAL SOCIETY
INSTITUTE

TWENTE SAFETY CAMPUS

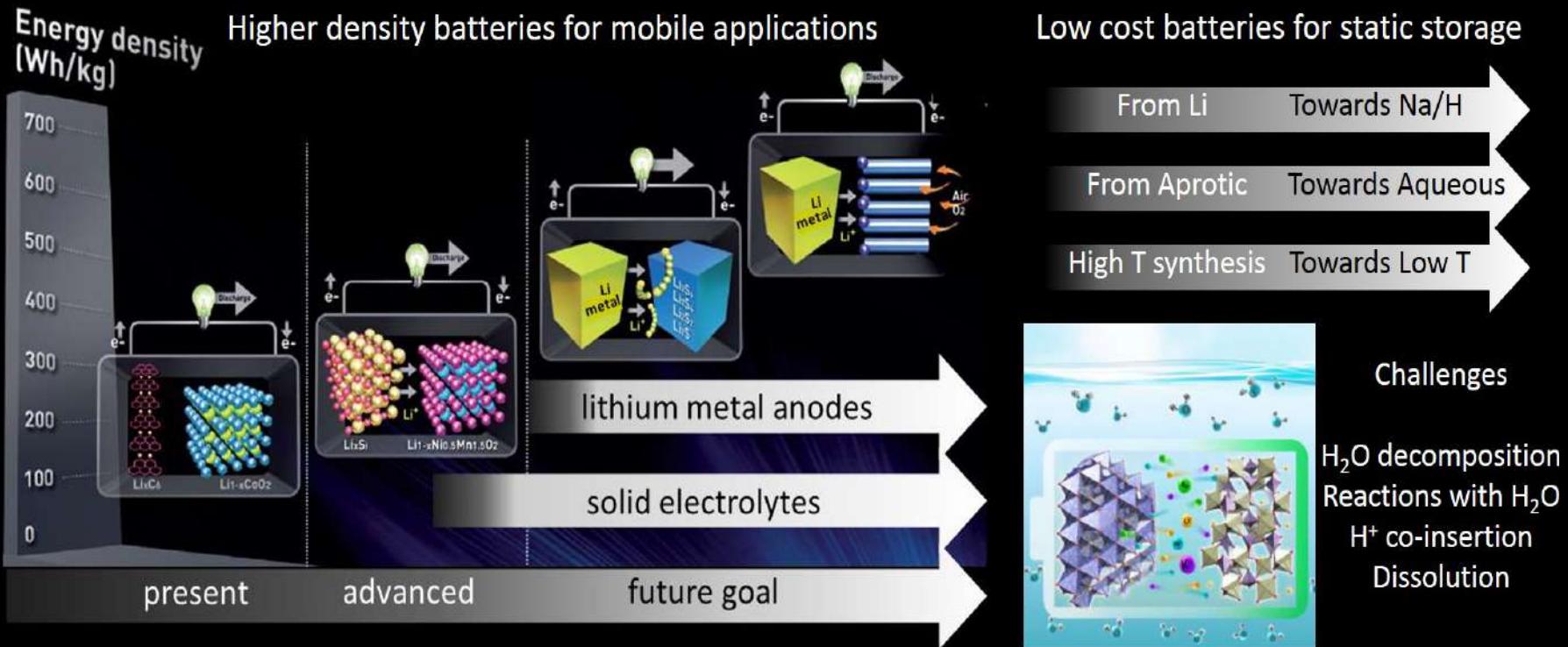
FRAUNHOFER
PROJECT CENTER@UT



Power Electronics

Battery Management System

Advanced materials for next-generation batteries



John B. Goodenough
97 years



M. Stanley Whittingham
78 years



Akira Yoshino
71 years



John B. Goodenough on October 9th 2019 :
“Don't retire too early !”

Prof. Mark Huijben, University of Twente

MESA⁺



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Thank you