SOLID STATE BATTERIES: A STORY ABOUT INTERFACES

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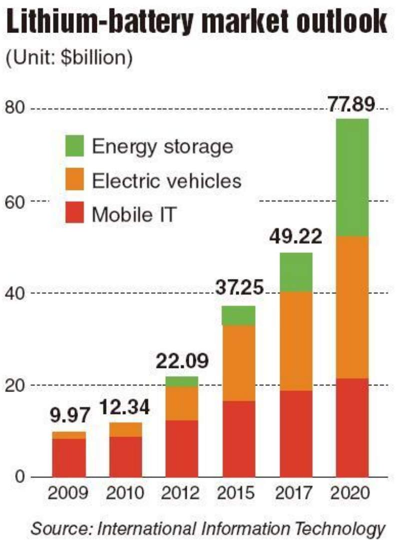
INTRODUCTION

LITHIUM ION BATTERIES…
IT ONLY JUST BEGAN REALLY

LITHIUM-ION BATTERY MARKET OUTLOOK

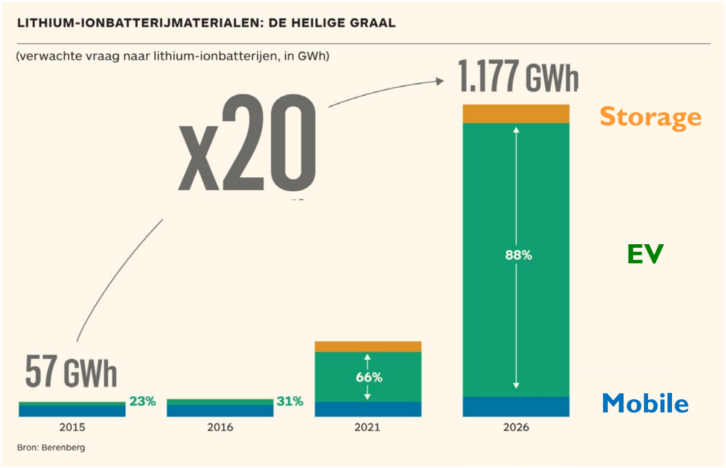
GROWTH POTENTIAL IS LARGE

- Fast growing Li-ion battery market because of emerging and growing technologies
  - Electrical will become the norm for automotive
  - Further growth of mobile electronics and new additions such as wearables and IOT



Source: International Information Technology

Steep growth in use of electric cars

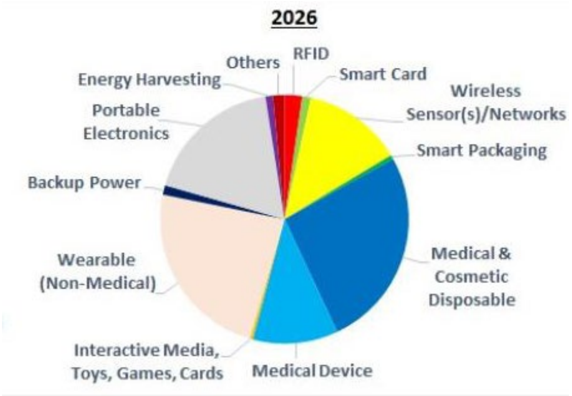

LITHIUM-IONBATTERIJMATERIALEN: DE HEILIGE GRAAL

(verwachte vraag naar lithium-ionbatterijen, in GWh)

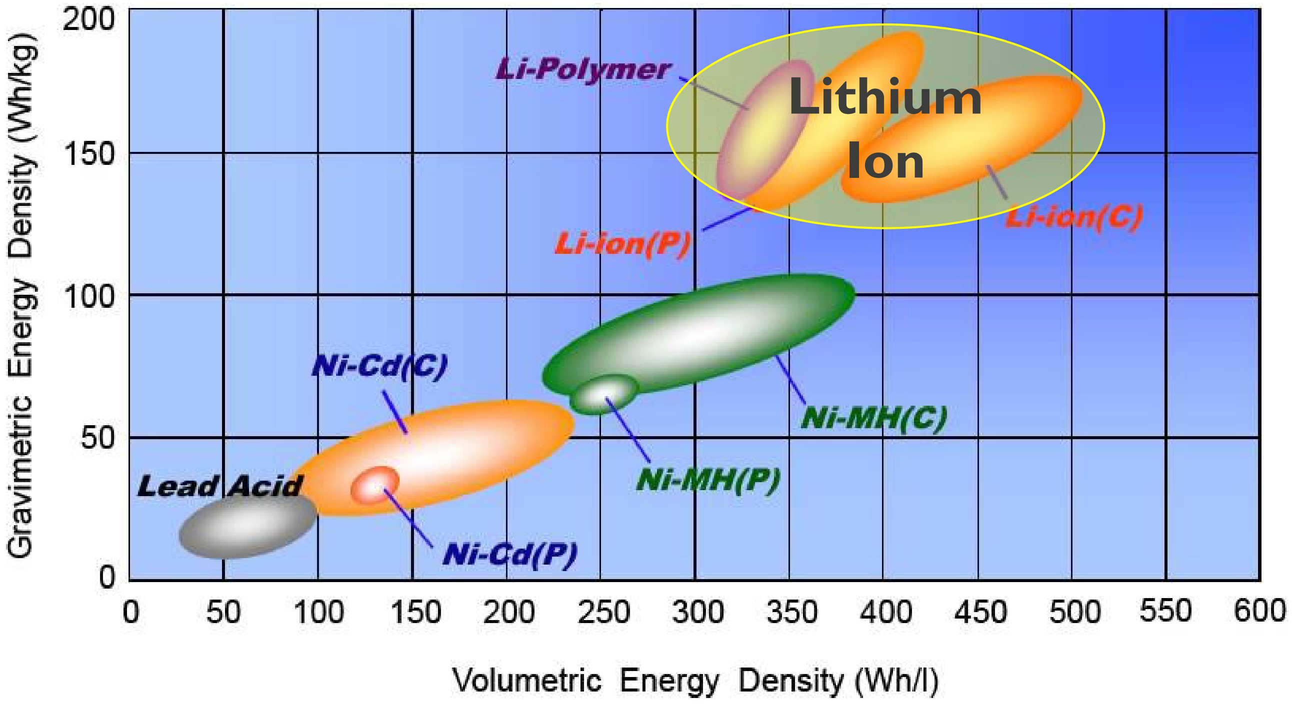
Bron: Berenberg

Source: De Tijd

New technologies coming



Li-ION CHEMISTRY HAS THE HIGHEST ENERGY DENSITY



Li-ion technology dominates rechargeable battery market for electronics

http://www.houseofbatteries.com/images/Comparison_chart.jpg

THE BATTERY IS OFTEN THE LIMITING FACTOR

The emergence of Li-ion battery has enabled new applications which emerged and evolved over the last decade...

High Energy density of Li-ion = portable energy source can be made small enough

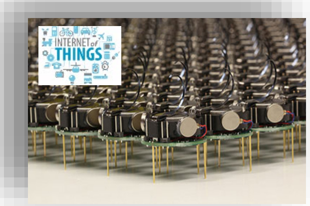
Portable electronics

Automotive

Storage

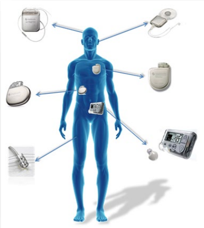
And will continue to do so for future electronics.

Form factor, Safety, and Fast charging are needed for future developments



IoT

Wearables



Health

Flexible electronics

APPLICATION SPECTRUM OF Li-ION BATTERIES

Rechargeable Li-ion batteries

Power on board

Back-up power chip or PCB

Portable electronics

Hobby and power tools

Vehicles

Bikes, automotive, aviation, rail,…

Wireless sensor networks

distributed wireless sensors and communicators…

Mobile-IT

Smart watch, phones, tablets, PC's

Renewable Energy

Home storage, micro-grid storage, grid storage

Wearable and Flexible

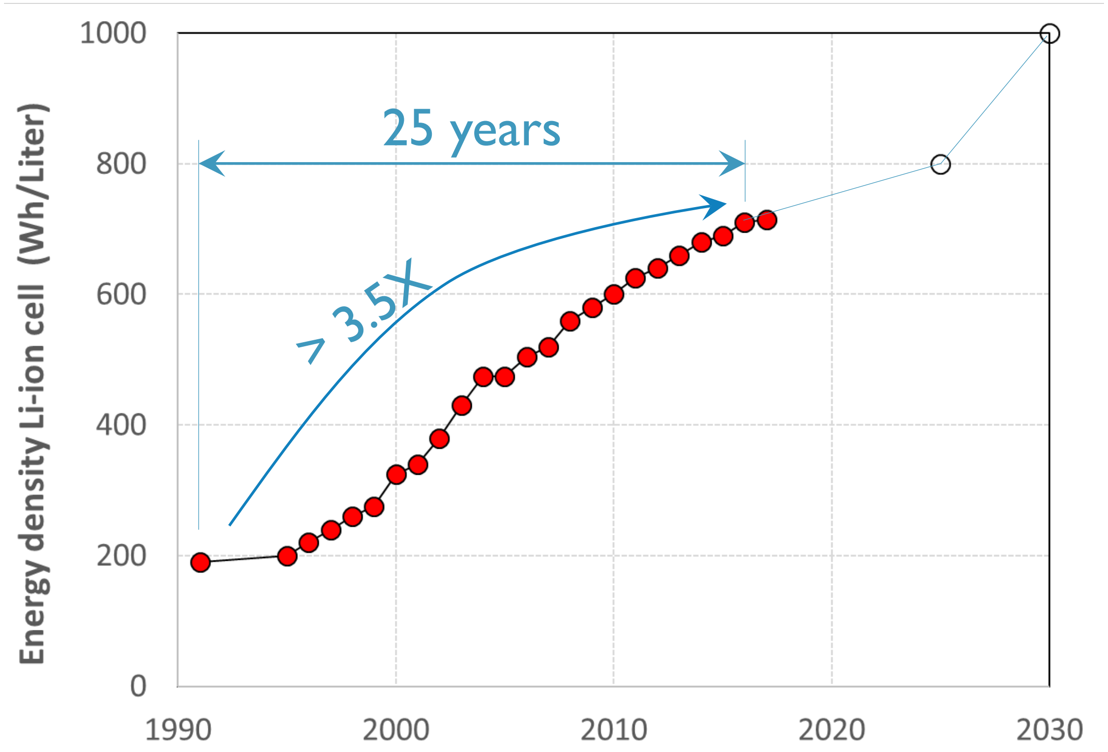
Smart carts, patches, wearables and flexible electronics…

< mWh < *< Wh <* *< kWh <* *< MWh*

1E-04 *1E-03* *1E-02* *1E-01* *1E+00* *1E+01* *1E+02* *1E+03* *1E+04* *1E+05* *1E+06*

EVOLUTION IN ENERGY DENSITY OF Li-ION CELL

AND FUTURE SET TARGETS BY INTERNATIONAL COMMUNITY



- Energy density of Li-ion cell has more than tripled in its 25 years of existence
- Further evolution of electrode materials and architectures will continue

ENERGY STORAGE NEEDS

IT IS MORE THAN ENERGY DENSITY ONLY

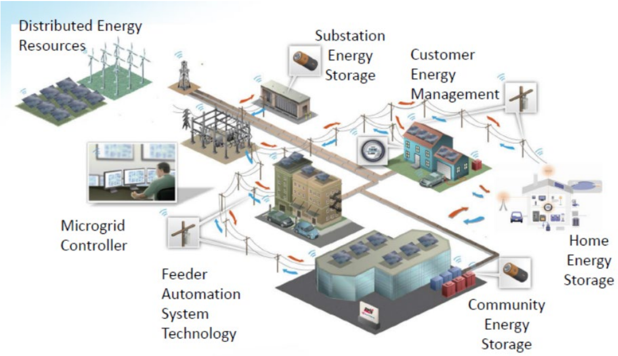
Mobile

Energy density
Fast recharging
Safe
Form factor
Cost
Long life time

EV

Energy density
Fast recharging
Safe
Long life time
Cost
Form factor

GRID



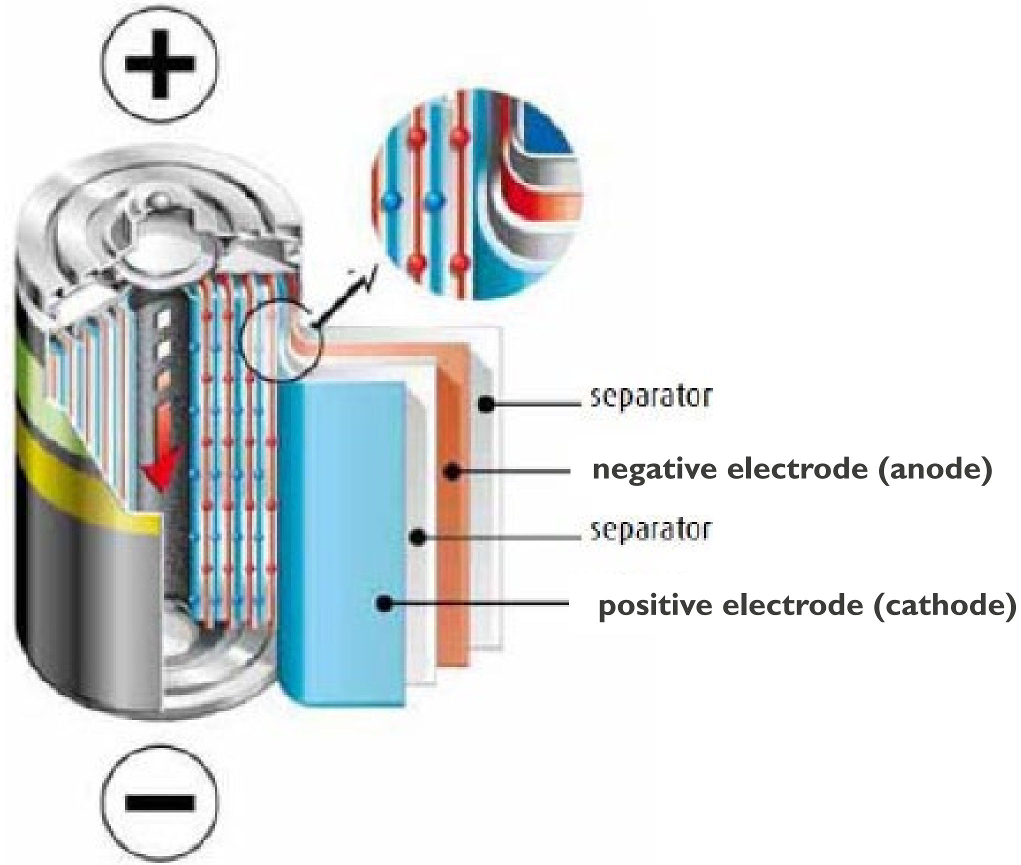
Safe
Long life time
Cost
Sustainable
High Energy density
Fast charging
Form factor

More to less important

BUT FIRST,
BACK TO THE BASICS

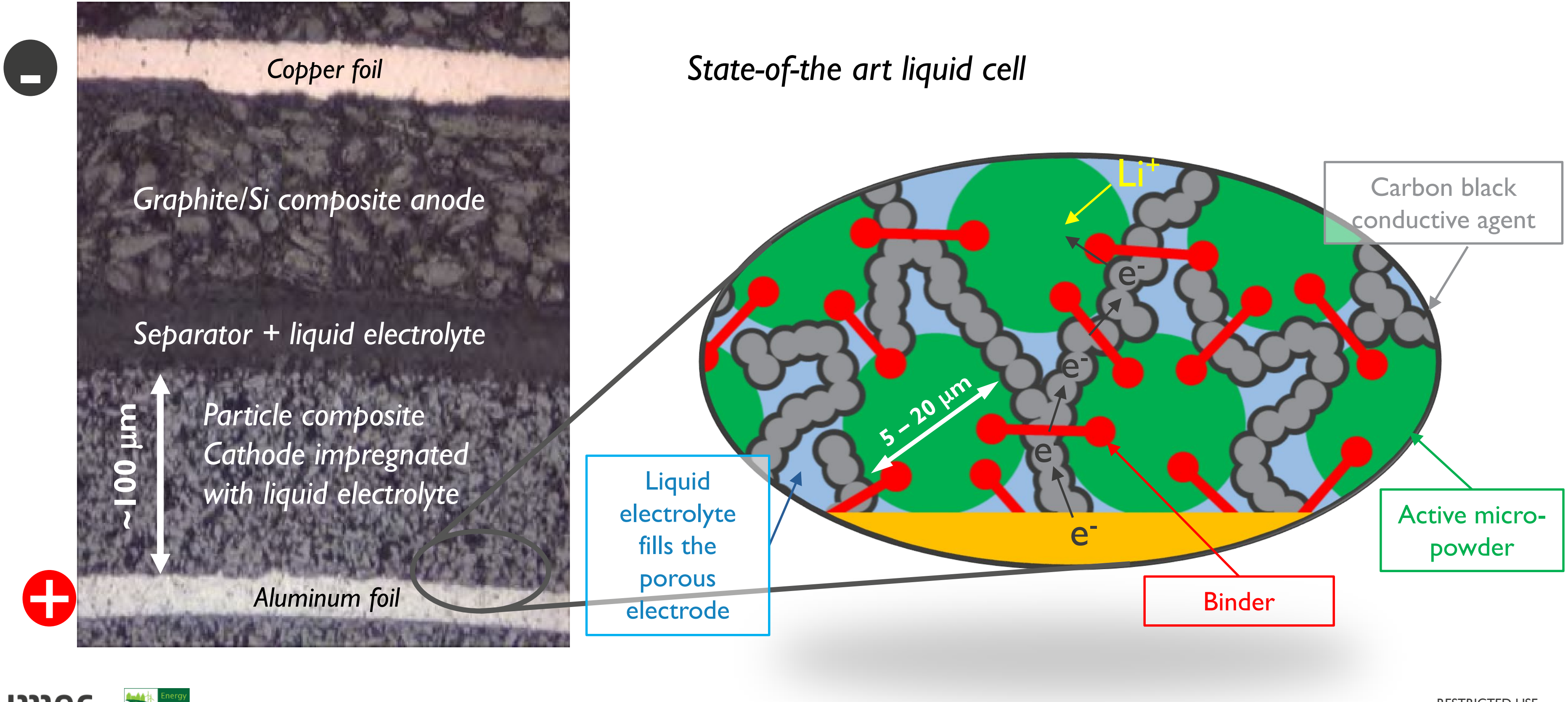
Li-ION BATTERY CELL

THE COMPONENTS



LITHIUM ION CELL WITH LIQUID ELECTROLYTE

THE CELL IS LITERALLY SOAKED WITH LIQUID ELECTROLYTE SOLUTION



-

+

Copper foil

Graphite/Si composite anode

Separator + liquid electrolyte

~100 µm

Particle composite Cathode impregnated with liquid electrolyte

Aluminum foil

State-of-the art liquid cell

Li^+

e^-

e^-

e^-

e^-

5 – 20 µm

Carbon black conductive agent

Liquid electrolyte fills the porous electrode

Binder

Active micro-powder

MATERIALS TODAY

+

Cathode Material	**V vs. Li^+/Li**	**Gravimetric Capacity**	**Volumetric Capacity**
$LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ (NCA)	3.8 V	180-200 Ah/kg	800-890 Ah/L
$LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ (NMC)	3.9V	160-170 Ah/kg	760-810 Ah/L
$LiCoO_2$ (LCO)	3.9 V	140 Ah/kg	710 Ah/L
$LiFePO_4$ (LFP)	3.4 V	170 Ah/kg	610 Ah/L
$LiMn_2O_4$ (LMO)	4.1 V	148 Ah/kg	650 Ah/L

Liquid Electrolytes

- lithium salts, such as **$LiPF_6$,** $LiBF_4$ or $LiClO_4$ in an organic solvent, such as ethylene carbonate, **dimethyl carbonate, diethyl carbonate**, propylene carbonate and mixtures thereof.
- typical conductivity of about 6-10mS/cm at RT
- the solvent decomposes on initial charging and forms a solid layer at the anode called the solid electrolyte interphase (SEI).

-

Anode Material	**V vs. Li^+/Li**	**Gravimetric Capacity**	**Volumetric Capacity**
$Li_4Ti_5O_{12}$ (LTO)	1.55V	160 Ah/kg	650 Ah/L
$Li_{4.4}Si$ (silicon)*	0.27 V	3580 Ah/kg	2190 Ah/L
LiC_6 (graphite)	0.15 V	370 Ah/kg	840 Ah/L

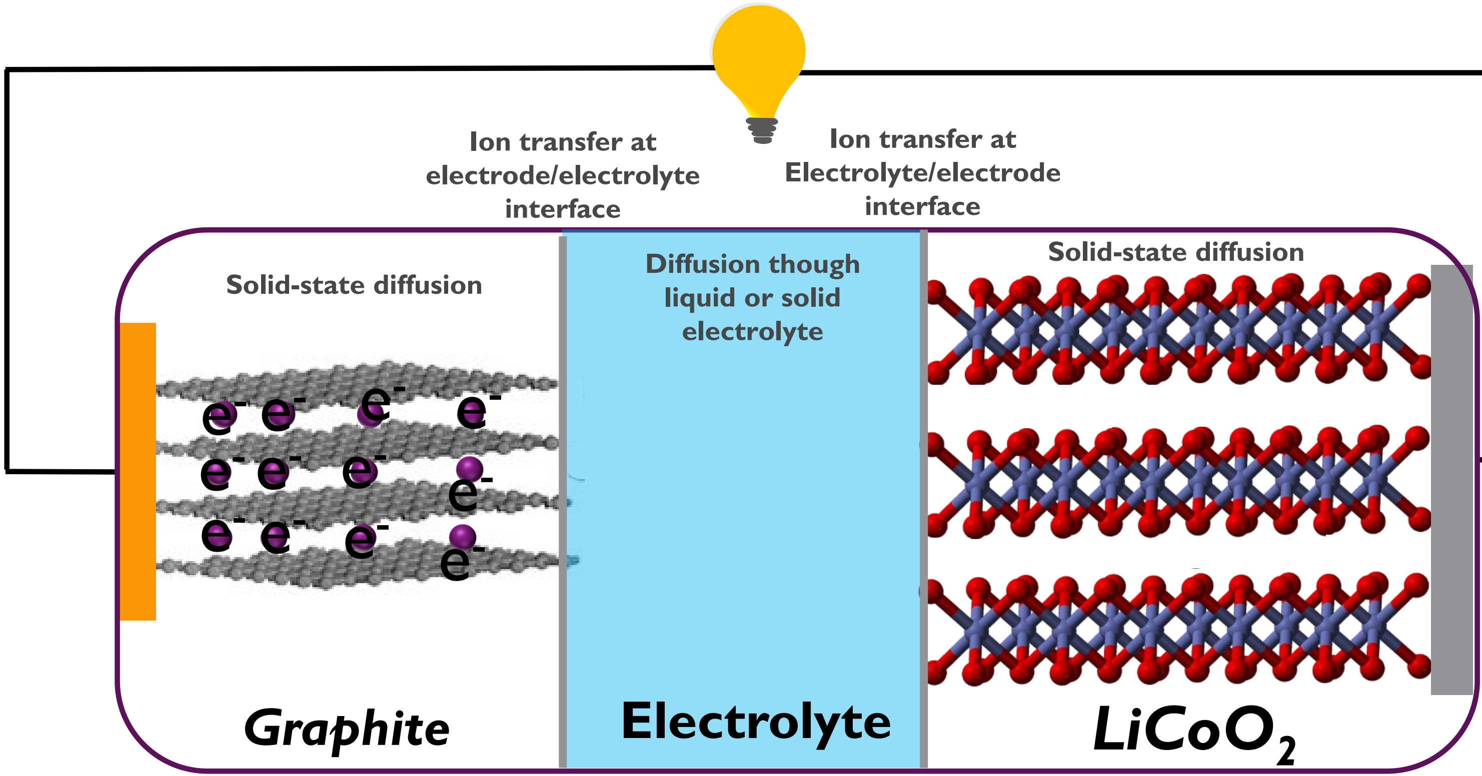
* Currently, only composites of Si(<10%) with graphitic carbon are commercially available

Cell voltage of 3.7V

Cell voltage of 3.6V

Li-ION CELL WORKS BY "ION INTERCALATION"

SOLID-STATE ELECTROCHEMISTRY AT WORK



Ion transfer at electrode/electrolyte interface

Ion transfer at Electrolyte/electrode interface

Solid-state diffusion

Diffusion though liquid or solid electrolyte

Solid-state diffusion

Graphite

Electrolyte

$LiCoO_2$

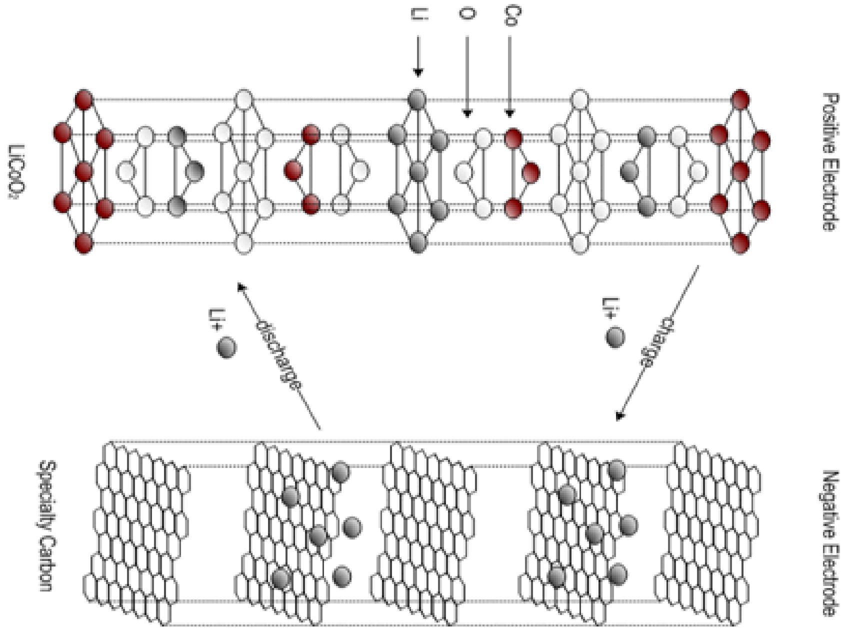
Negative Electrode
(0.15V)

Positive Electrode
(3.9V)

● Li^+ ion
e^- electron

THE ROLE OF Li^+ ION IS MAINTAIN ELECTRONEUTRALITY

UPON OXIDATION IN ANODE AND REDUCTION IN THE CATHODE



Oxidized state with valence of Cobalt (+IV)

Reduced state with valence of Cobalt (+III)

$$Li_{1-x}CoO_2 + xLi^+ + xe^- \leftrightharpoons LiCoO_2$$

$$-(\,C_6 + xLi^+ + xe^- \leftrightharpoons Li_xC_6\,)$$

+

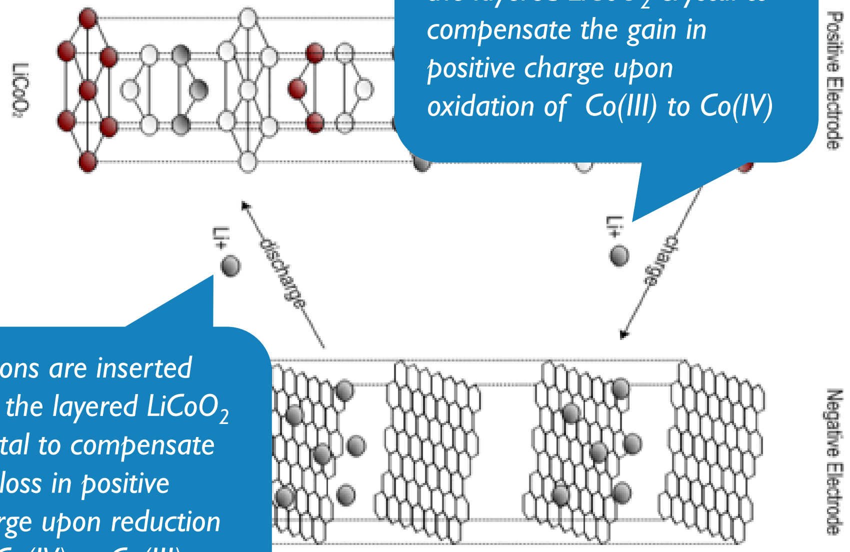
Cell reaction: $Li_{1-x}CoO_2 + Li_xC_6 \leftrightharpoons LiCoO_2 + C_6$

Charged state (electrochemical potential difference of ~ 3.7eV)

Dis-charged state (electrochemical potential difference of ~ 0 eV)

THE ROLE OF Li^+ ION IS MAINTAIN ELECTRONEUTRALITY

UPON OXIDATION IN ANODE AND REDUCTION IN THE CATHODE



Li^+ ions are extracted from the layered $LiCoO_2$ crystal to compensate the gain in positive charge upon oxidation of Co(III) to Co(IV)

Li^+ ions are inserted into the layered $LiCoO_2$ crystal to compensate the loss in positive charge upon reduction of Co(IV) to Co(III)

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Charged state (electrochemical potential difference of ~ 3.7eV)

Dis-charged state (electrochemical potential difference of ~ 0 eV)

$Li_{1-x}CoO_2$ Layered structure

Co(IV) ←→ Li(I)Co(III)

(NMC and NCA active materials have layered structure as well)

$LiMO_2$ structures are ordered derivatives of rock salt (ordering occurs along alternate 111 layers)

Li intercalates into octahedral sites between the edge sharing CoO_2 layers

Good electrical conductor

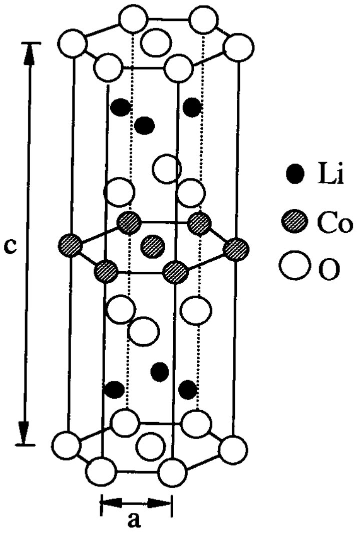
Lithium de-intercalation varies from $0 \geq x \geq 0.5$ and is reversible

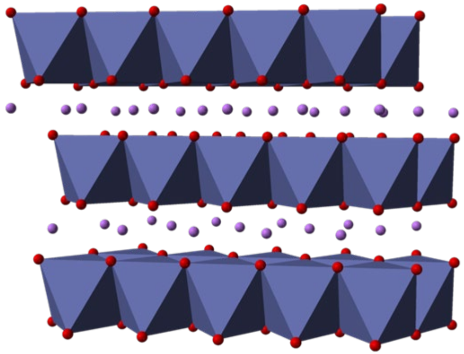
Capacity ~ 45 A -h/kg

Voltage ~ 3.7 Volts

Energy density ~ 165 W -h/kg

Cobalt is expensive (relative to Ti, Ni and Mn).





Anisotropic lithiation kinetics (depends on crystal orientation)!

$Li_{1-x}Mn_2O_4$ spinel structure

Mn(IV) ←→ Li(I)Mn(III)

Structure type is defect spinel

Mn ions occupy the octahedral sites, while Li^+ resides on the tetrahedral sites.

Rather poor electrical conductivity

Lithium de-intercalation varies from $0 \geq x \geq 1$, comparable to $Li_{1-x}CoO_2$

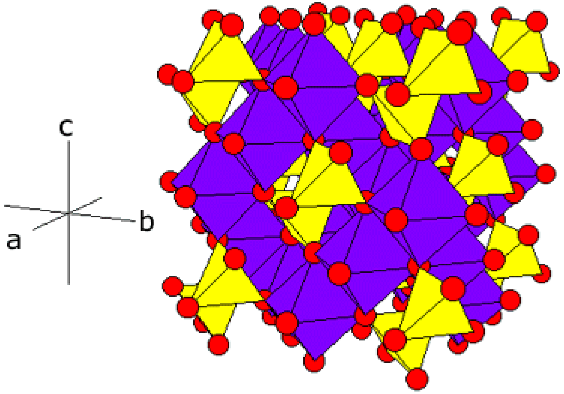
Presence of Mn^{3+} gives a Jahn-Teller distortion that limits cycling. High Li content stabilizes layer like structure.

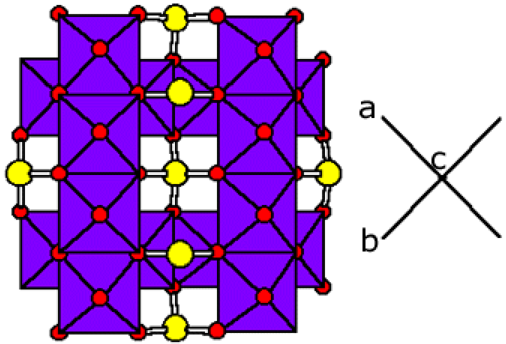
Capacity ~ 36 A -h/kg

Voltage ~ 3.8 Volts

Energy density ~ 137 W -h/kg

Mn is cheap and non-toxic.

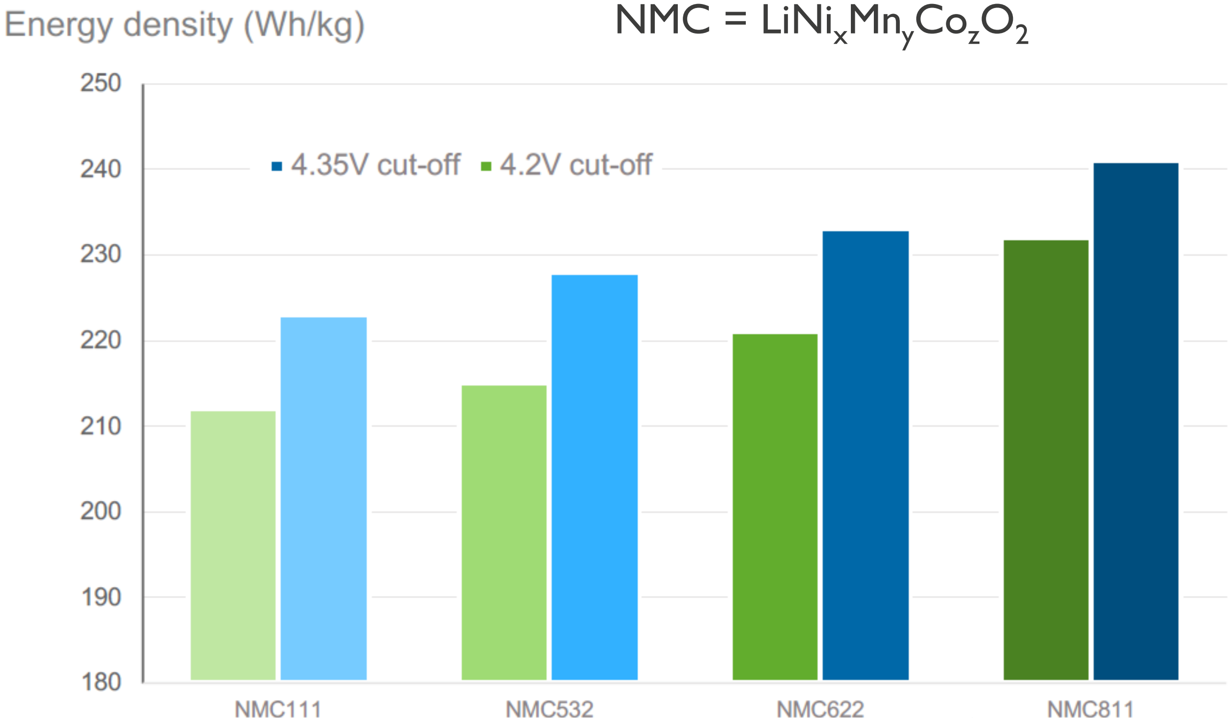




Lithiation kinetics independent on crystal orientation

Energy density increasing strategies

NMC = $LiNi_xMn_yCo_zO_2$



Increasing Ni content

- *Ni-rich cathode materials have higher capacity – but are more reactive and unstable*
- *Increasing the cut-off voltage gives more accessible lithium, but electrolyte stability issues*

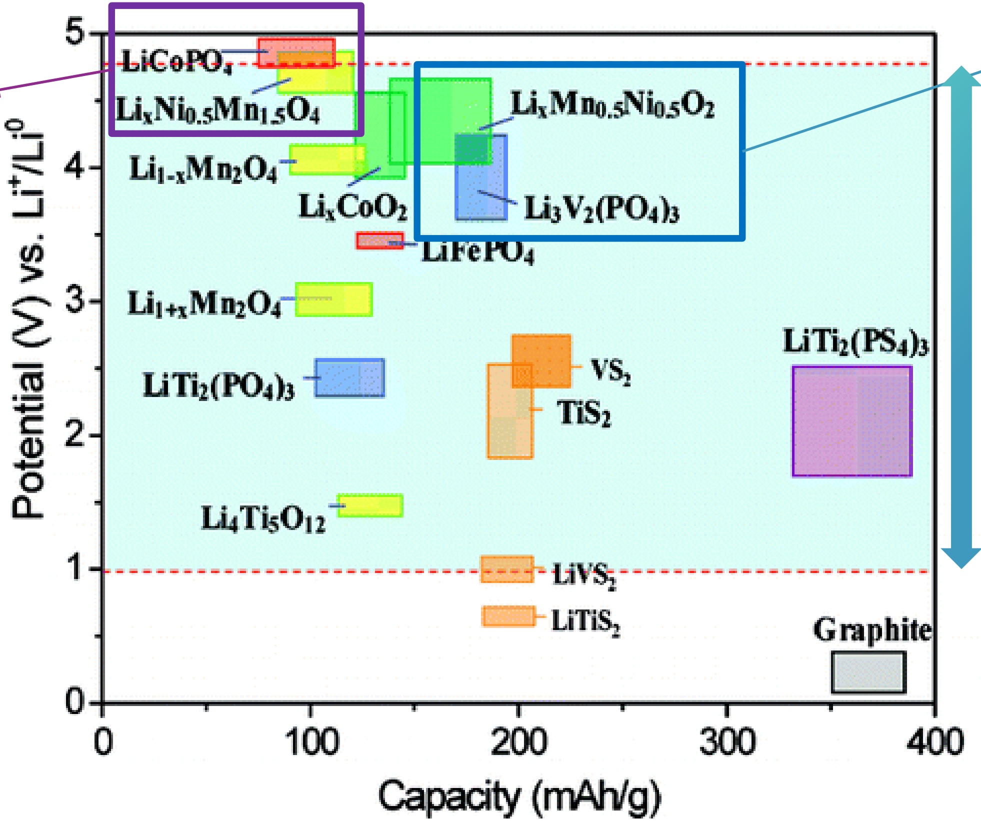
Source: Kurt Vandeputte (Umicore), ITF presentation, 23-24 May 2018, Antwerp, Belgium

NEXT GENERATION HIGH ENERGY CATHODE MATERIALS

“5V” cathode materials

For increased energy

Issues with <u>electrolyte</u> stability



Electrochemical window of liquid carbonate electrolyte

Li-rich cathode materials

For increased capacity

Issues with <u>electrode</u> stability

Current anodes are not stable against the liquid carbonate electrolyte – however the decomposition product forms a so-called SEI layer (solid-electrolyte interphase) which blocks further decomposition and as such effectively widens the electrochemical window

* Goodenough et al., 2010 (DOI: 10.1021/cm901452z)

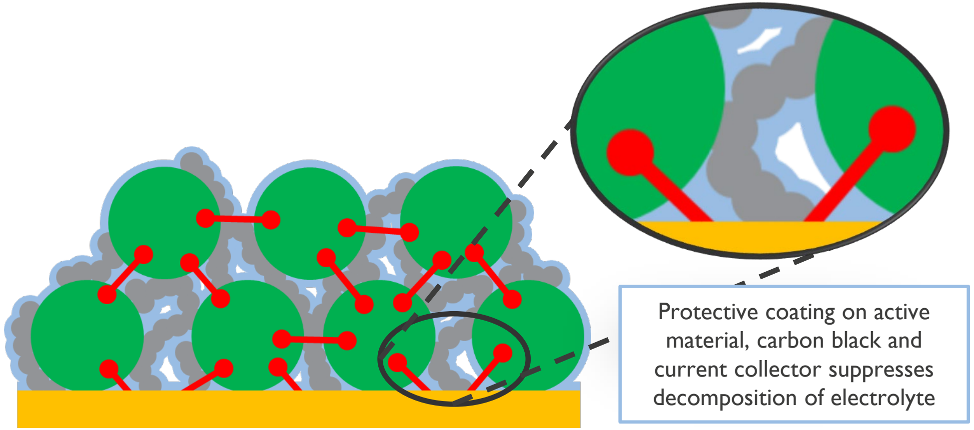
(SUB)NANOMETER THIN ARTIFICIAL INTERPHASES

ALD/MLD SYSTEMS FOR COATING INSIDE THE POROUS ELECTRODES

- Thin artificial interphase layers are deposited as protective buffer layers in the porous electrodes to enhance battery performance and life-time
- Imec also works on novel thin-film materials for added functionality in the electrode (dual conductor materials)

ALD/MLD Picosun R200 integrated in glovebox

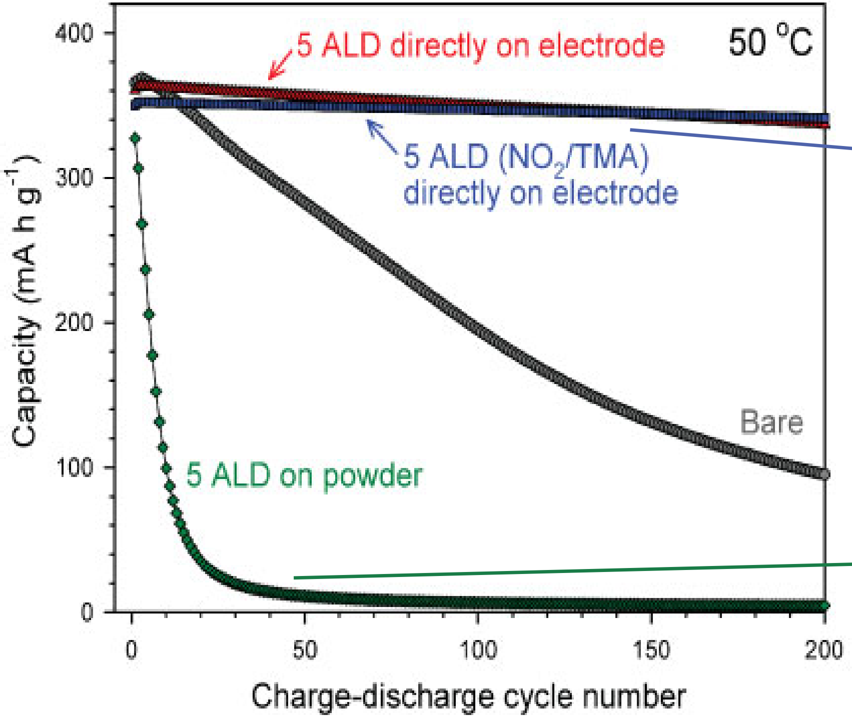
Oxides and Li-compounds

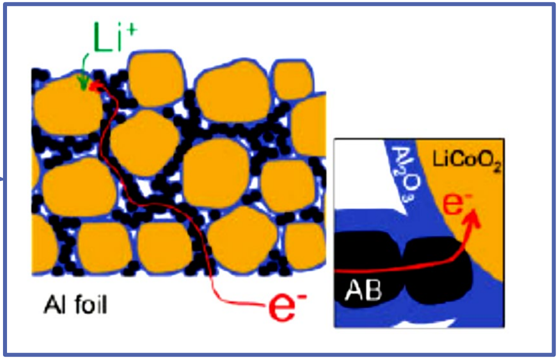


Protective coating on active material, carbon black and current collector suppresses decomposition of electrolyte

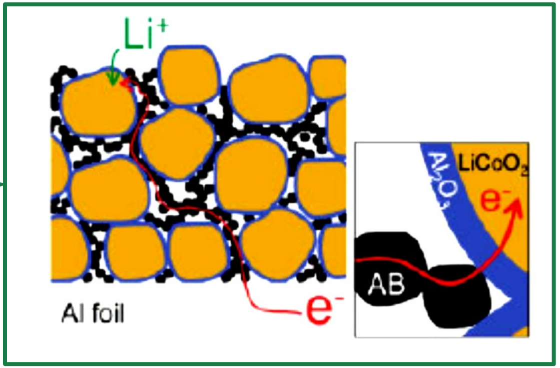
Al_2O_3 IS THE MOST COMMONLY APPLIED PROTECTIVE COATING

(FIRST) Al_2O_3 COATING OF $LiCoO_2$





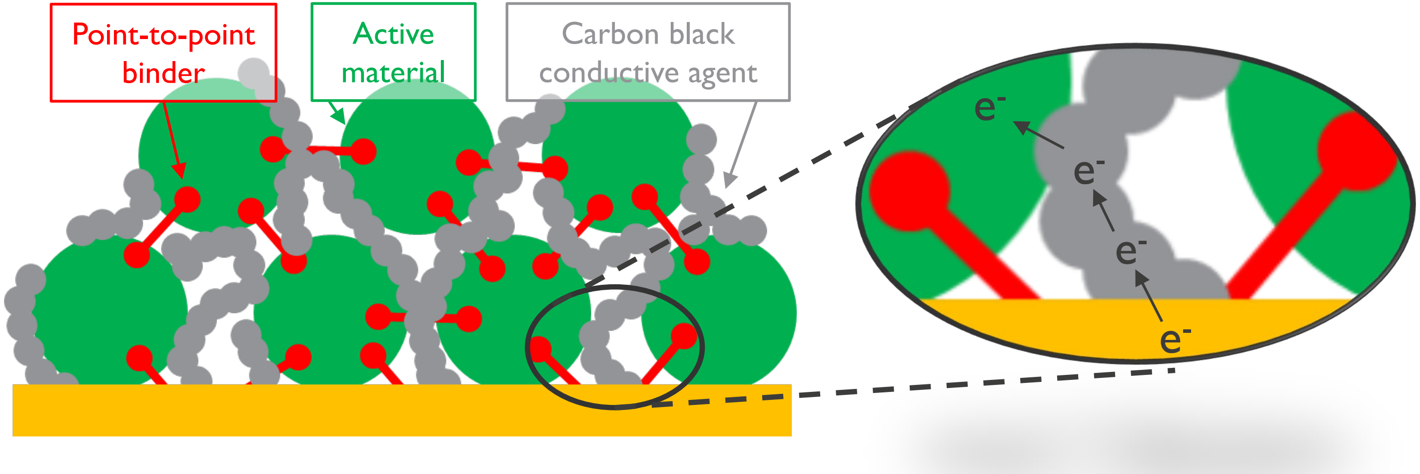
- Al_2O_3 coating on the full electrode greatly improves cyclability → attributed to the formation of a artificial CEI



- Al_2O_3 coating directly on particles blocks electronic access
- Coating cannot be made too thick as Al_2O_3 is an ionic insulator

TOO SMALL EC WINDOW LEADS TO DECOMPOSITION ELECTROLYTE

DECOMPOSITION ELECTROLYTE RESULTS IN INTERFACE DEGRADATION



- The decomposition (oxidation) of electrolyte at high voltage electrodes such as $LiNi_{0.5}Mn_{1.5}O_2$ (LNMO) result in the formation on undesired interphase layers – known as Cathode Electrolyte Interface (CEI) layers.
- The CEI layers form on both the active electrode and carbon conductive additive (which is at the same potential)
- These electronically insulating layers eventually hinder electrons from flowing from
  - the carbon black to the active material and/or
  - the current collector to the carbon black

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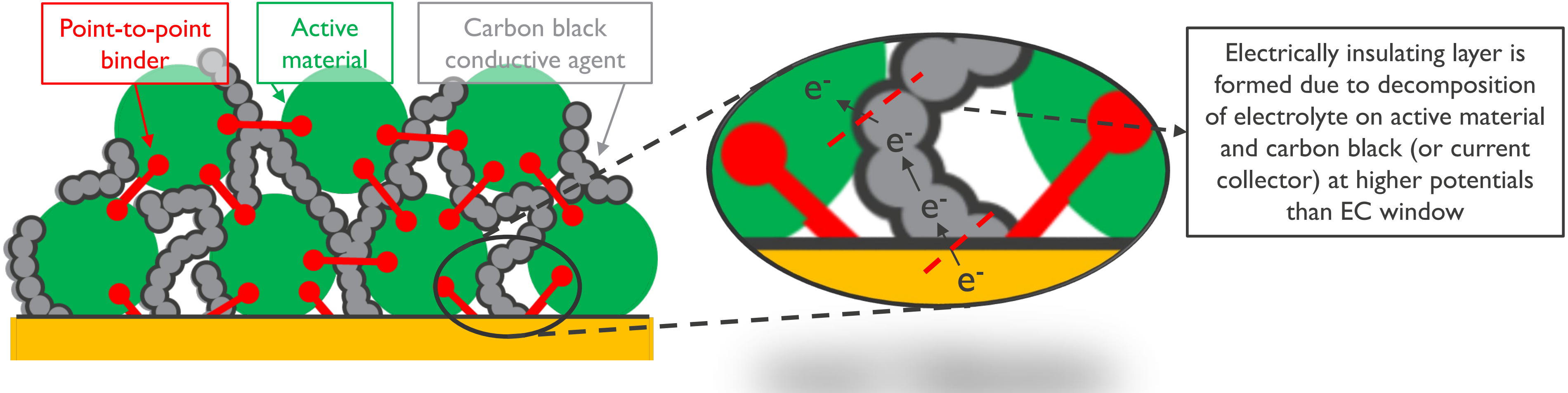

Electrically insulating layer is formed due to decomposition of electrolyte on active material and carbon black (or current collector) at higher potentials than EC window

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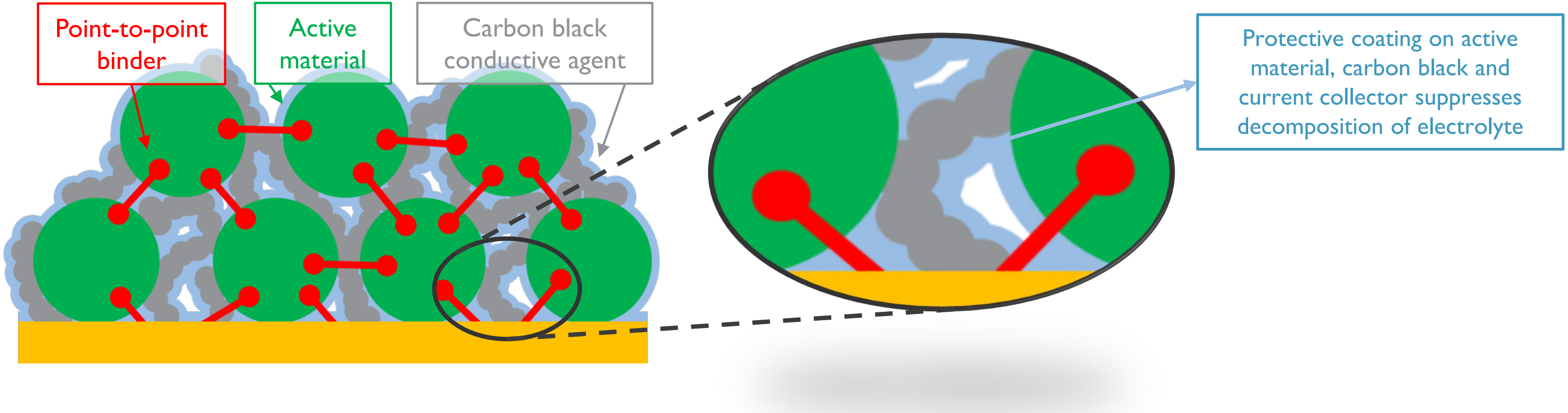
PROTECTIVE COATINGS HELP AGAINST INTERFACE DEGRADATION

ALD/MLD FOR COATING INSIDE THE POROUS ELECTRODES



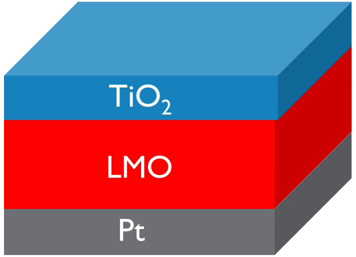
Protective coating on active material, carbon black and current collector suppresses decomposition of electrolyte

- Solution: deposition of “artificial interphase” layers to prevent the formation of decomposition layer and maintain good electrical contact for good battery performance and life time.

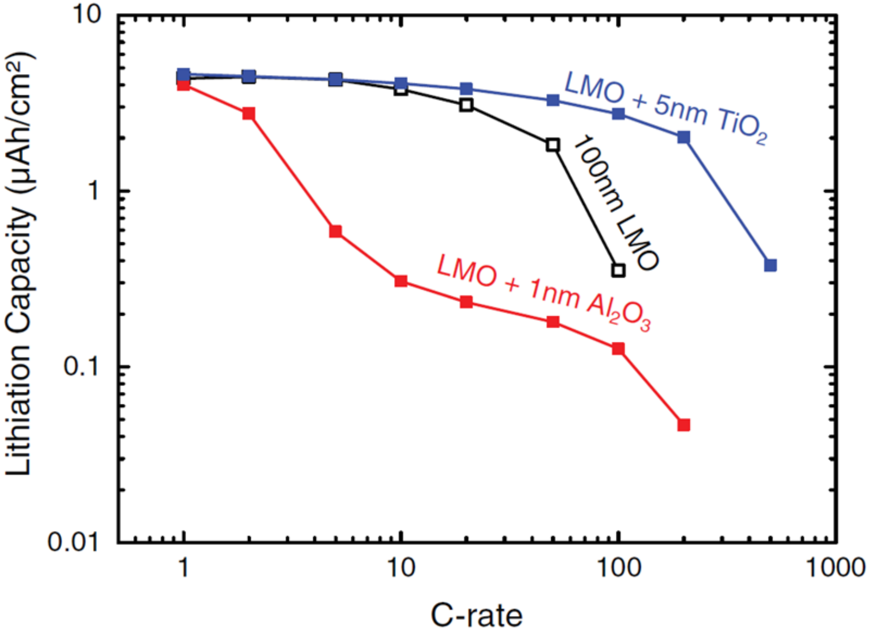
TiO_2 IS IONICALLY AND ELECTRONICALLY CONDUCTIVE

SO DOES NOT INHIBIT ION TRANSPORT

- Planar thin-film models showed that 5nm TiO_2 protective coating layer still does not inhibit rate performance whereas 1nm Al_2O_3 does



Felix Mattelaer, Philippe M. Vereecken, Jolien Dendooven, and Christophe Detavernier, *Adv. Mater. Interfaces*, 1601237 (2017). DOI:10.1002/admi.201601237

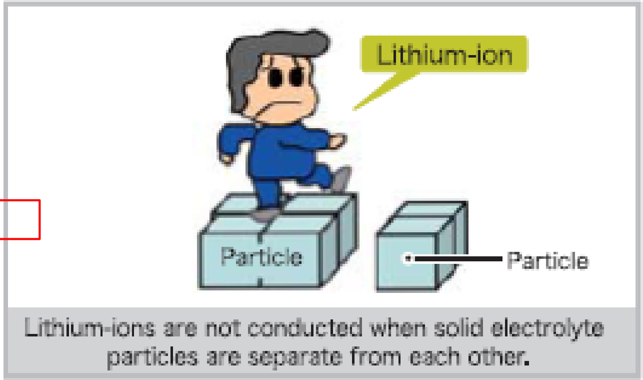


Thin model systems are used to investigate interfaces and buffer layers as artificial interphases – see presentation "Battery Interface platform"

BLOCKING INTERFACES AND INTERPHASES

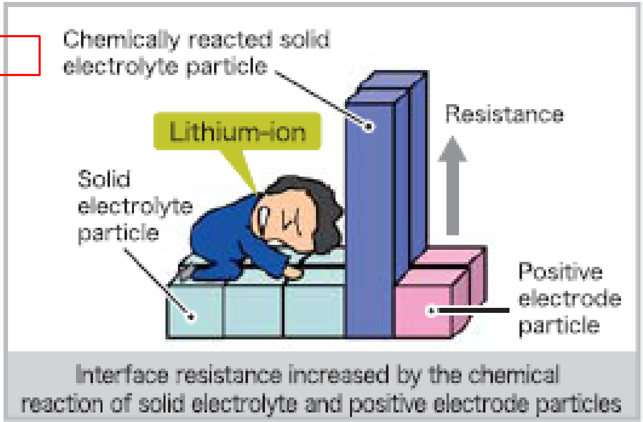
STILL A MAJOR ISSUE ALSO FOR SOLID-STATE BATTERIES

Disconnected INTERFACES

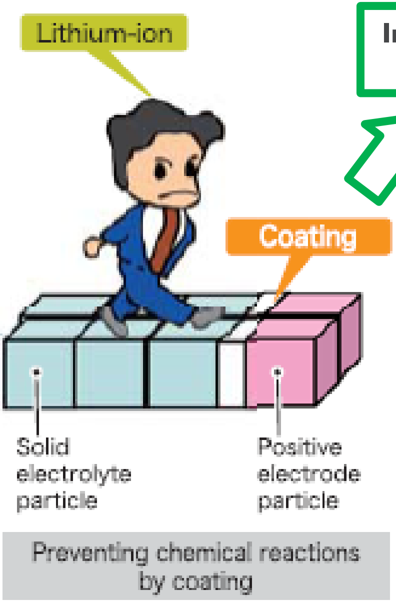


Lithium-ions are not conducted when solid electrolyte particles are separate from each other.

Un-intentional INTERPHASE layer



Interface resistance increased by the chemical reaction of solid electrolyte and positive electrode particles



Preventing chemical reactions by coating

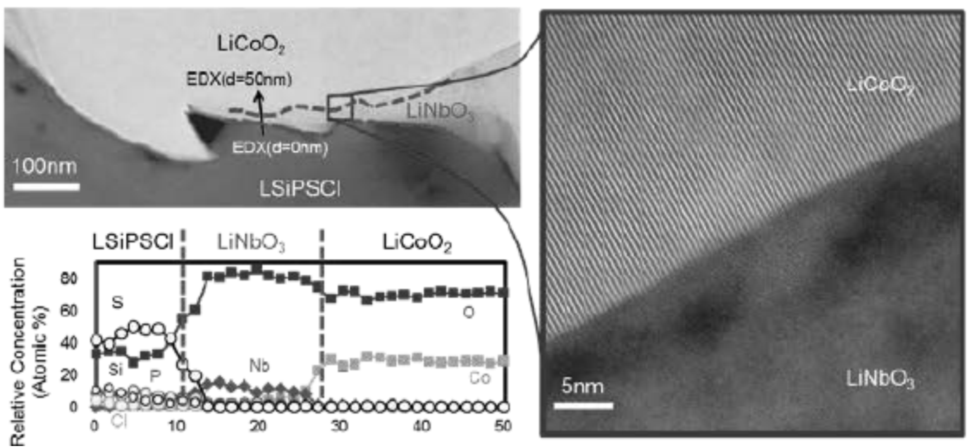
Intentional or artificial INTERPHASE layer

(source: Toyota R&D announcement)

SOLID STATE BATTERIES STILL REQUIRE PROTECTIVE COATINGS

EXAMPLE TOYOTA 2016

Kato et *al*., Nat. Ener., 2016



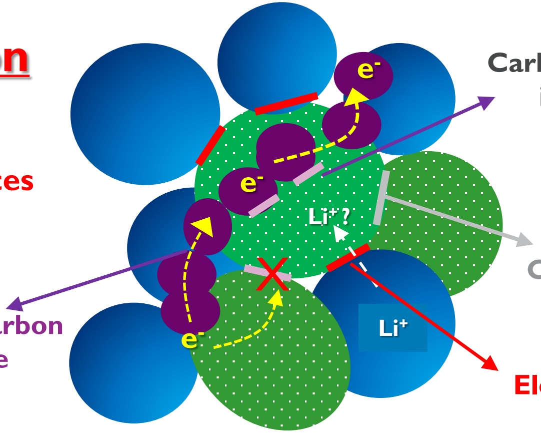
- $LiCoO_2$ cathode reacts with sulfide solid electrolyte ($Li_{9.5}Si_{1.7}P_{1.4}S_{11.7}Cl_{0.3}$)
- $LiNbO_3$ coated $LiCoO_2$ prevents direct reaction with the electrolyte
  - Enabling battery functionality
  - $LiNbO_3$ is good ion conductor but poor electronic conductor (bandgap 4 eV)

THIN-FILM MODEL SYSTEM

TO STUDY INTERFACES AND INTERPHASES

Powder composite electrode

Zillion
poorly defined interfaces



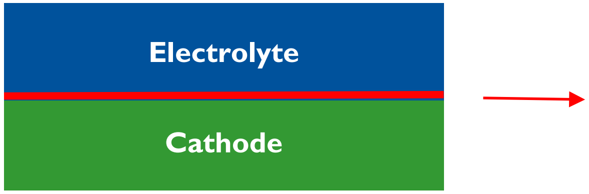
Carbon-Cathode interface

Cathode/Cathode interface

Electrolyte/Cathode interface

Carbon – Carbon interface

Thin-film model system



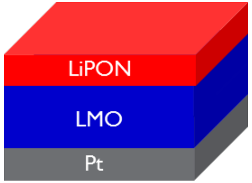
One
well-defined interface

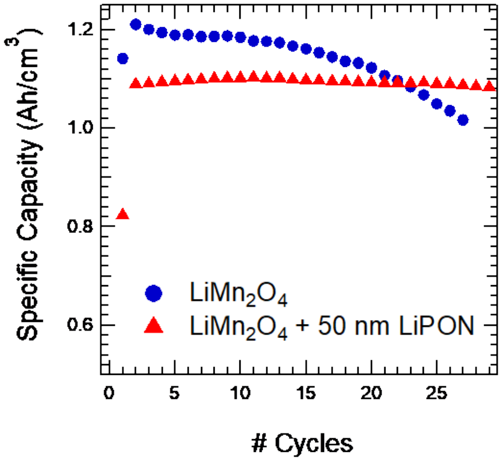
We make experimental model systems using thin film deposition (PVD, ALD) and patterning to simulate and optimize the individual interfaces and to extract kinetic and transport properties which can be input for theoretical models

TF MODEL SYSTEMS ARE USED TO STUDY INTERFACES AND BUFFER LAYERS

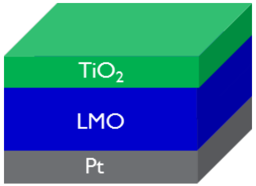
PROTECTIVE COATING TO ENHANCE ELECTRODE CYCLABILITY AND RATE PERFORMANCE

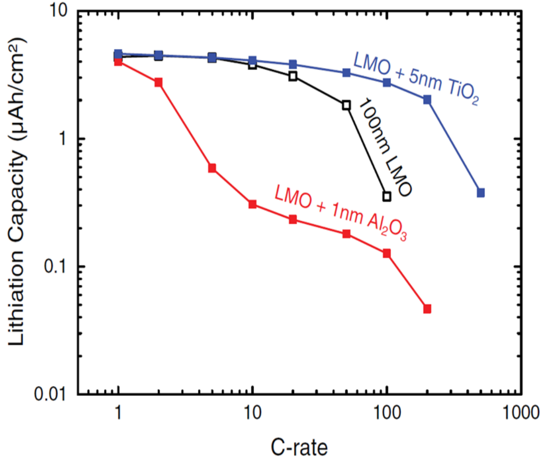
- Planar thin-film model systems are used to study interfaces and buffer layers
  - Thin-film LiPON coating on $LiMn_2O_4$ cathode improves cyclability by preventing Mn^{3+} dissolution
  - Thin-film am-TiO_2 coating on LMO enhances the rate performance





B. Put, P. M. Vereecken, N. Labyedh, A. Sepulveda, C. Huyghebaert, I. P. Radu, and A. Stesmans, ACS Appl. Mater. Interfaces, 2015. DOI: 10.1021/acsami.5b06386



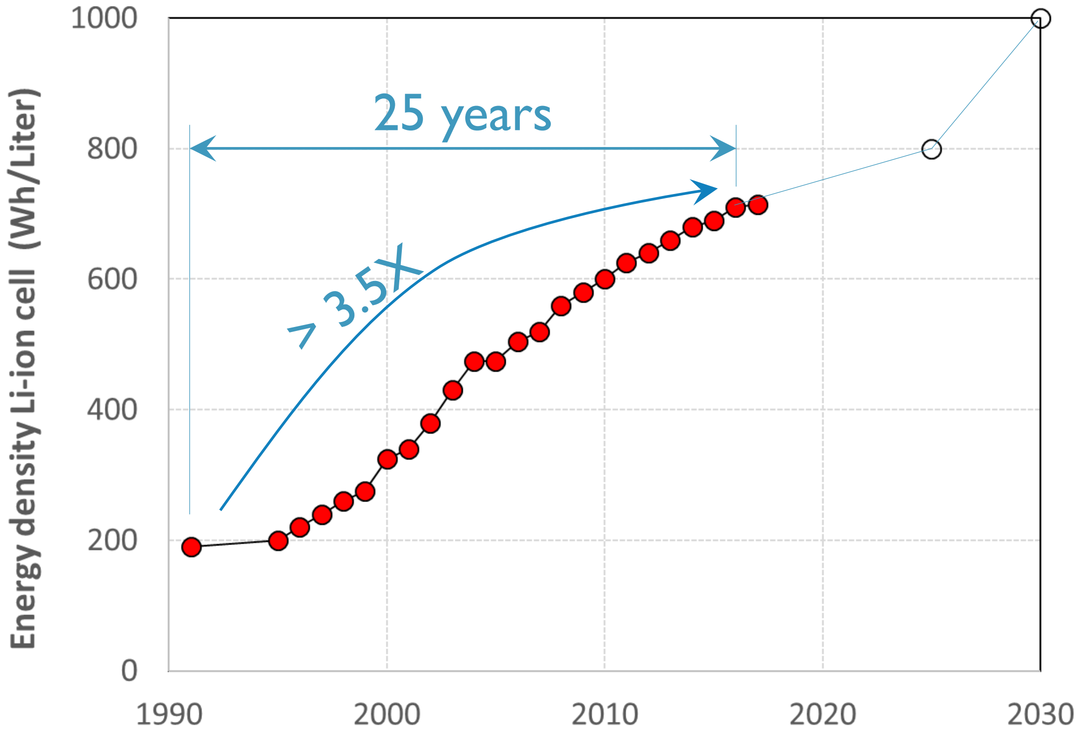


Felix Mattelaer, Philippe M. Vereecken, Jolien Dendooven, and Christophe Detavernier, *Adv. Mater. Interfaces*, 1601237 (2017). DOI:10.1002/admi.201601237

SOLID-STATE AND LITHIUM METAL FOR NEXT GENERATION BATTERIES

EVOLUTION IN ENERGY DENSITY OF Li-ION CELL

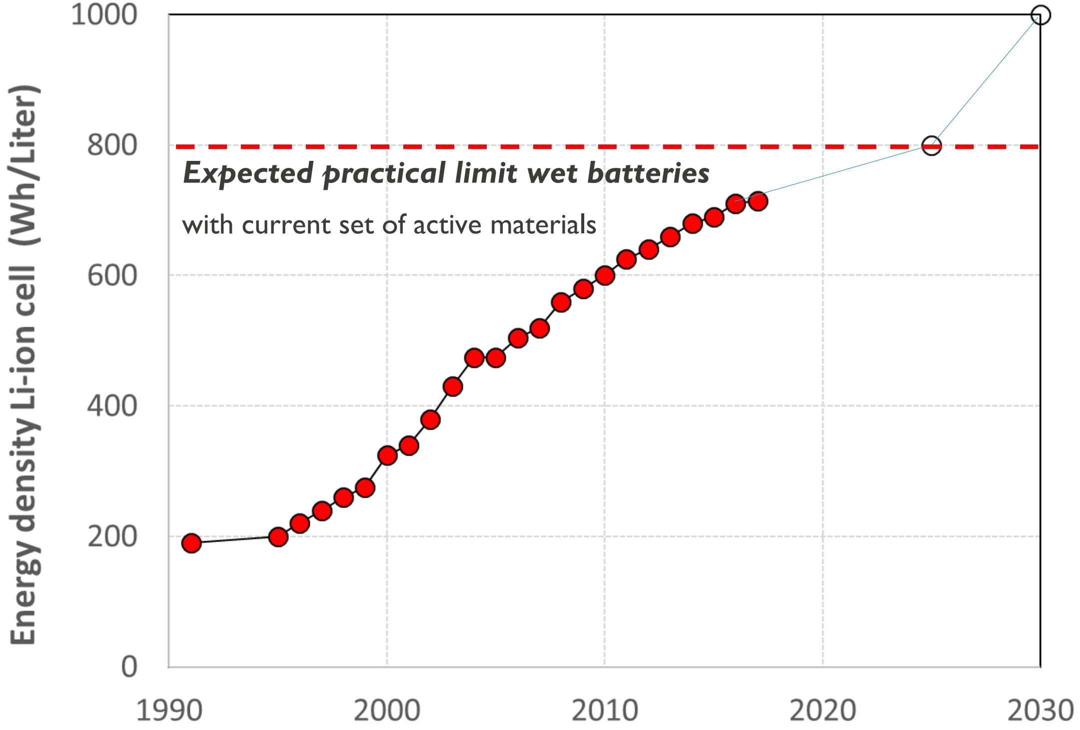
AND FUTURE SET TARGETS BY INTERNATIONAL COMMUNITY



- Energy density of Li-ion cell has more than tripled in its 25 years of existence
- Further evolution of electrode materials and architectures will continue

EVOLUTION IN ENERGY DENSITY OF Li-ION CELL

AND FORESEEN ISSUES



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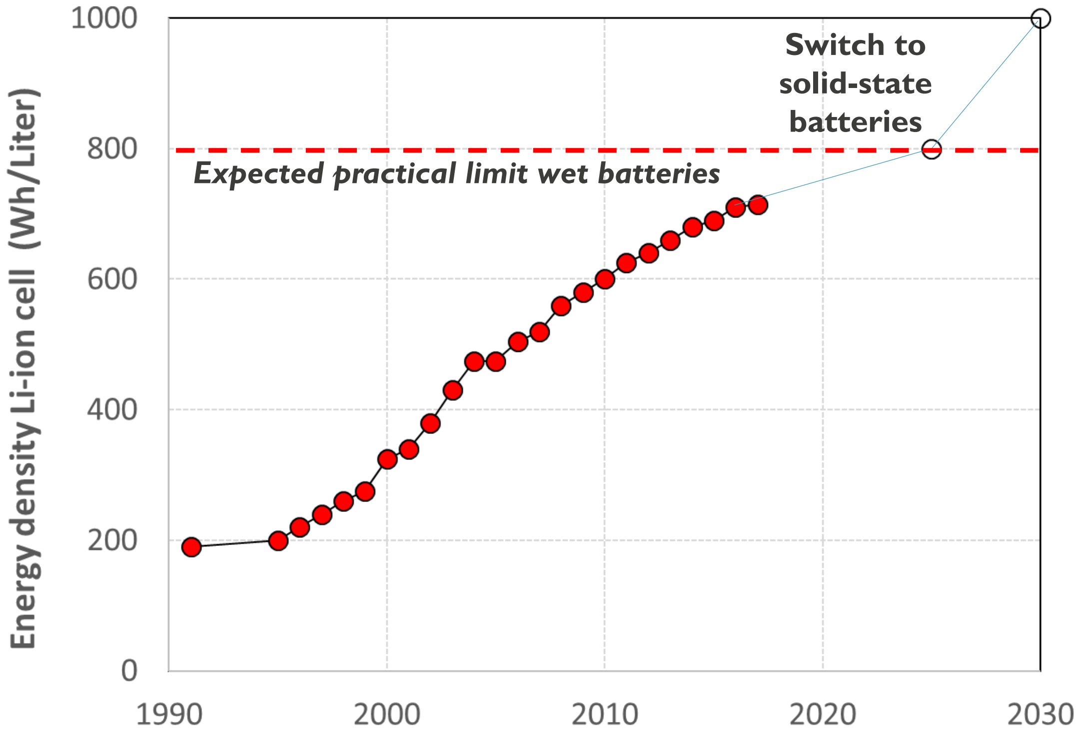
- Currently leveling off towards practical ceiling of 800Wh/L by 2025

EVOLUTION IN ENERGY DENSITY OF LI-ION CELL

AND ROADMAP TARGETS FOR 2025 AND 2030



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EVOLUTION IN ENERGY DENSITY OF LI-ION CELL

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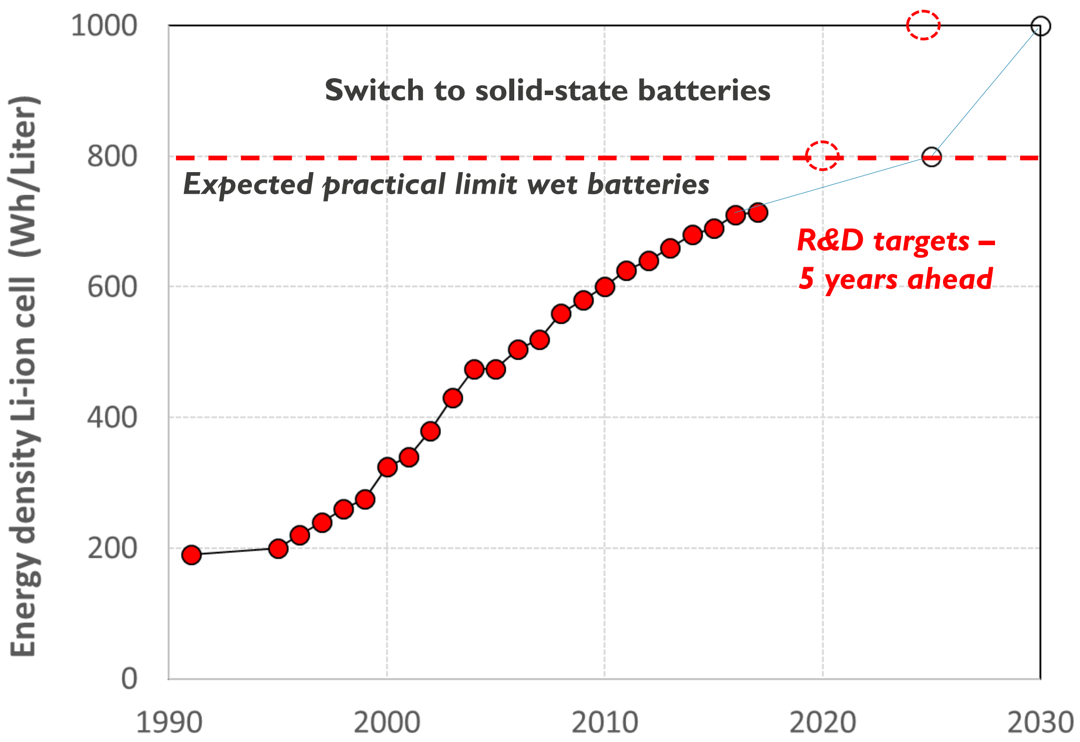

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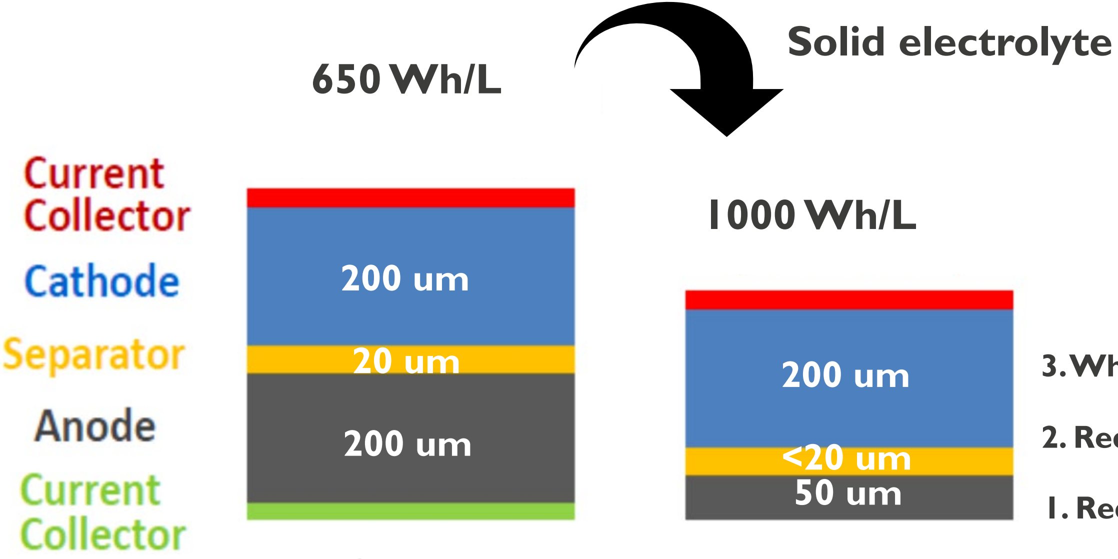
SOLID ELECTROLYTE ENABLES METALLIC LITHIUM

THE PRINCIPLE IS SIMPLE – CREATE MORE SPACE IN THE CELL ARCHITECTURE



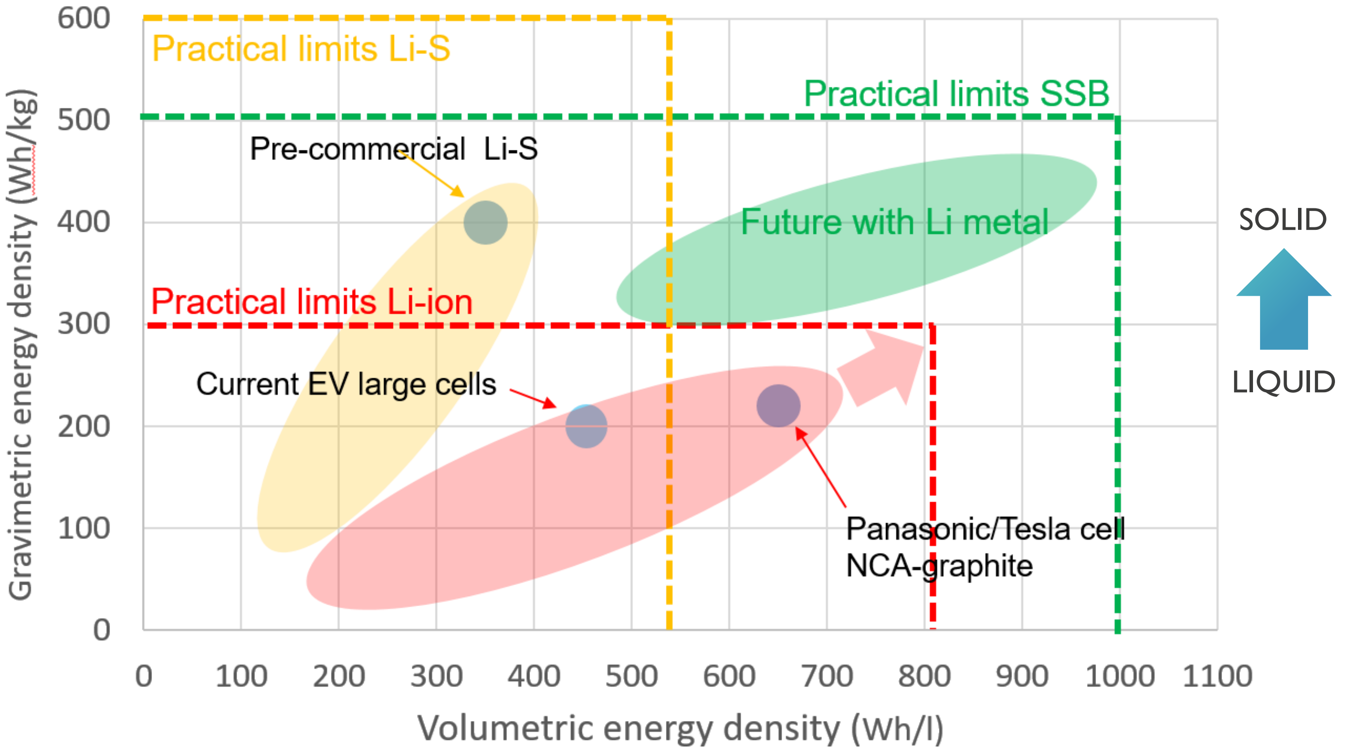
NMC cathode
Graphite anode

NMC cathode
Lithium anode

3. What about the cathode?
2. Reduction of "separator" thickness
1. Reduction of anode thickness

ELECTRODE MATERIAL SET PRACTICAL UPPER LIMIT

SOLID STATE EXTENDS THE PRACTICAL LIMIT FOR Li-ION CELLS



More cathode material can be stacked in same volume through change of cell architecture

- *Thinner (Li) anode*
- *Thinner separator*
- *Denser cathode?*

Source: Marcel Meeus and Stéphane Levasseur (Umicore)

SOLID STATE ENABLES NEXT GENERATION BATTERIES

WITH NANOTECHNOLOGY AND LI METAL ANODES

- Solid-state enables increase **energy and power density**
  - Through more efficient use of the space in cell and battery
  - Introduction of high voltage cathodes and lithium metal
- Solid-state provides **safety**
  - Elimination of the flammable solvent and of the risk of leakage (implants)
  - However still combustible and risk for poisoning
- Solid-state provides **form factor**
  - Easier to mold in shape required
  - Potential for down-sizing for micro-batteries

SAFETY

Removal of the flammable organic components


Laptop fire at conference


First fire in a Tesla Model S burns $600 million off the company's value


Samsung Galaxy S7

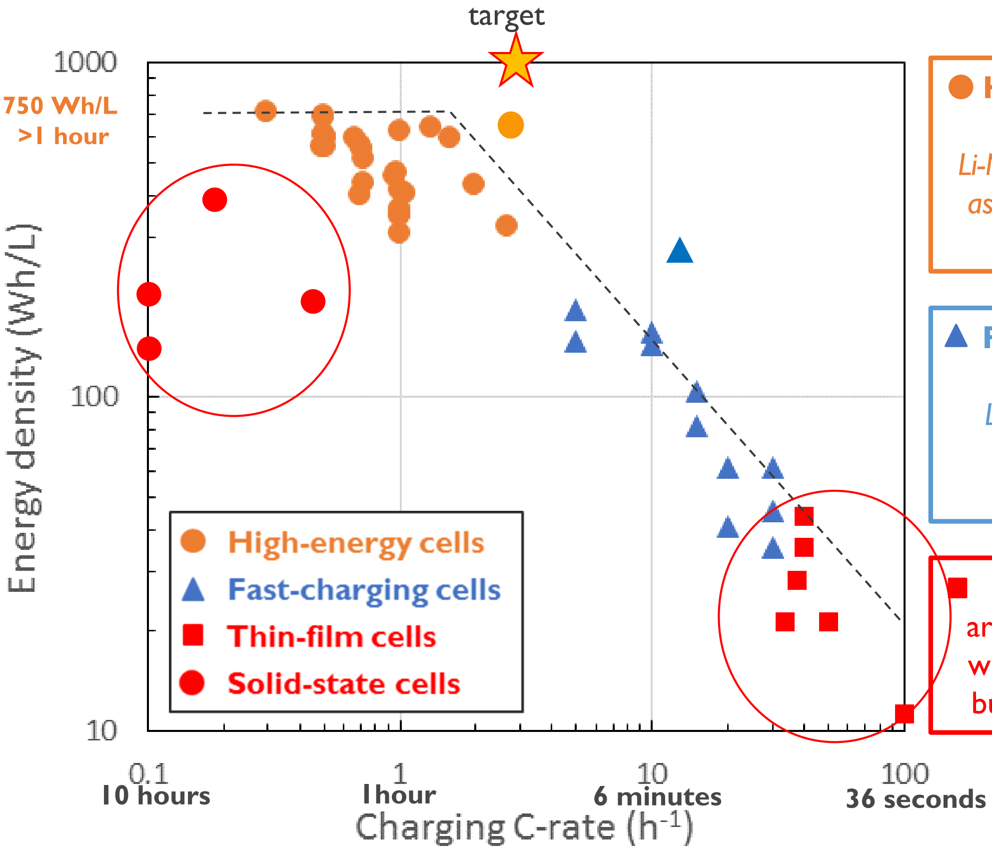

Boeing 787 Dreamliner grounded


Battery failure Fyra train


Hoverboard on fire

SOLID-STATE HAS STILL SOME CATCHING UP TO DO

● **Solid-state cells**
First generations of all-solid state cells with inorganic solid electrolyte have issues with rate performance



● **High-energy NMC cells (3.6V):**
Li-NiMnCo-oxide chemistry as cathode C/Si as anode and liquid electrolyte

▲ **Fast-charging LTO cells (2.4V):**
LiMn-oxide as cathode LiTi-oxide as anode and liquid electrolyte

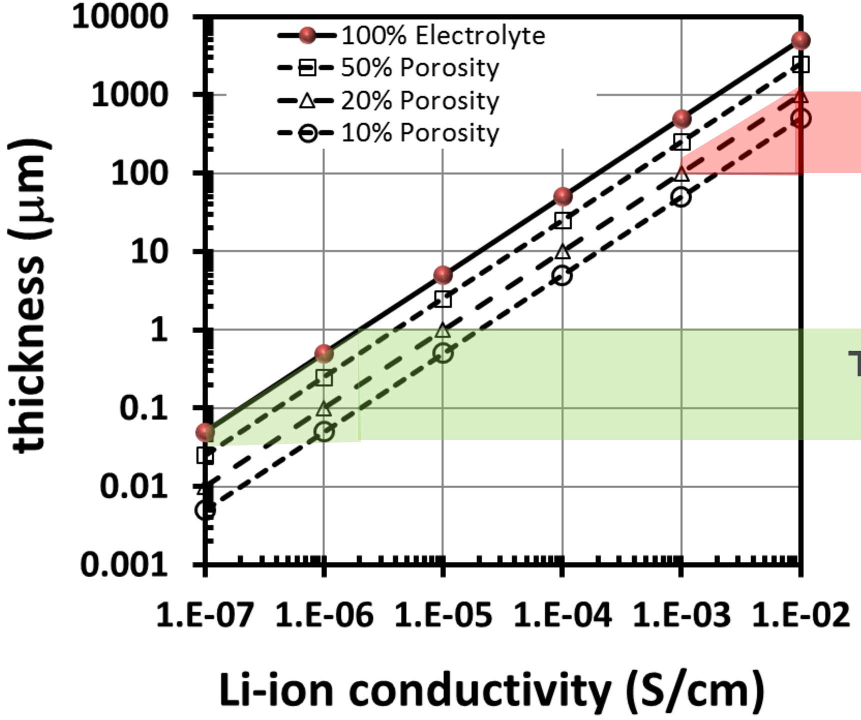
■ **Thin-film cells:**
are solid-state batteries which give fast charging but low energy density

IT STARTS WITH A SOLID ELECTROLYTE WITH GOOD ION CONDUCTIVITY

CONDUCTIVITY OF ELECTROLYTE DETERMINES ITS THICKNESS

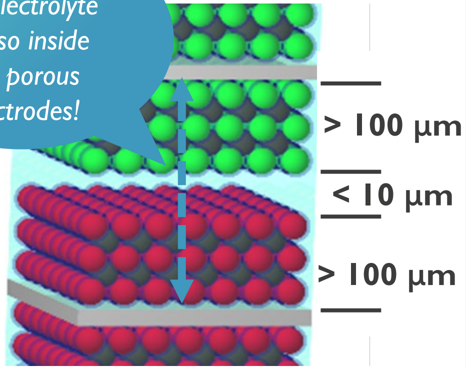
AND THUS THE POSSIBLE CELL ARCHITECTURE

For an maximum internal cell resistance of 50Ω.cm²

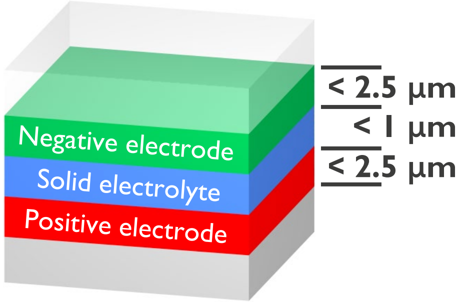


Powder battery
σ >10^{-3} S/cm

Don't forget, the electrolyte is also inside the porous electrodes!

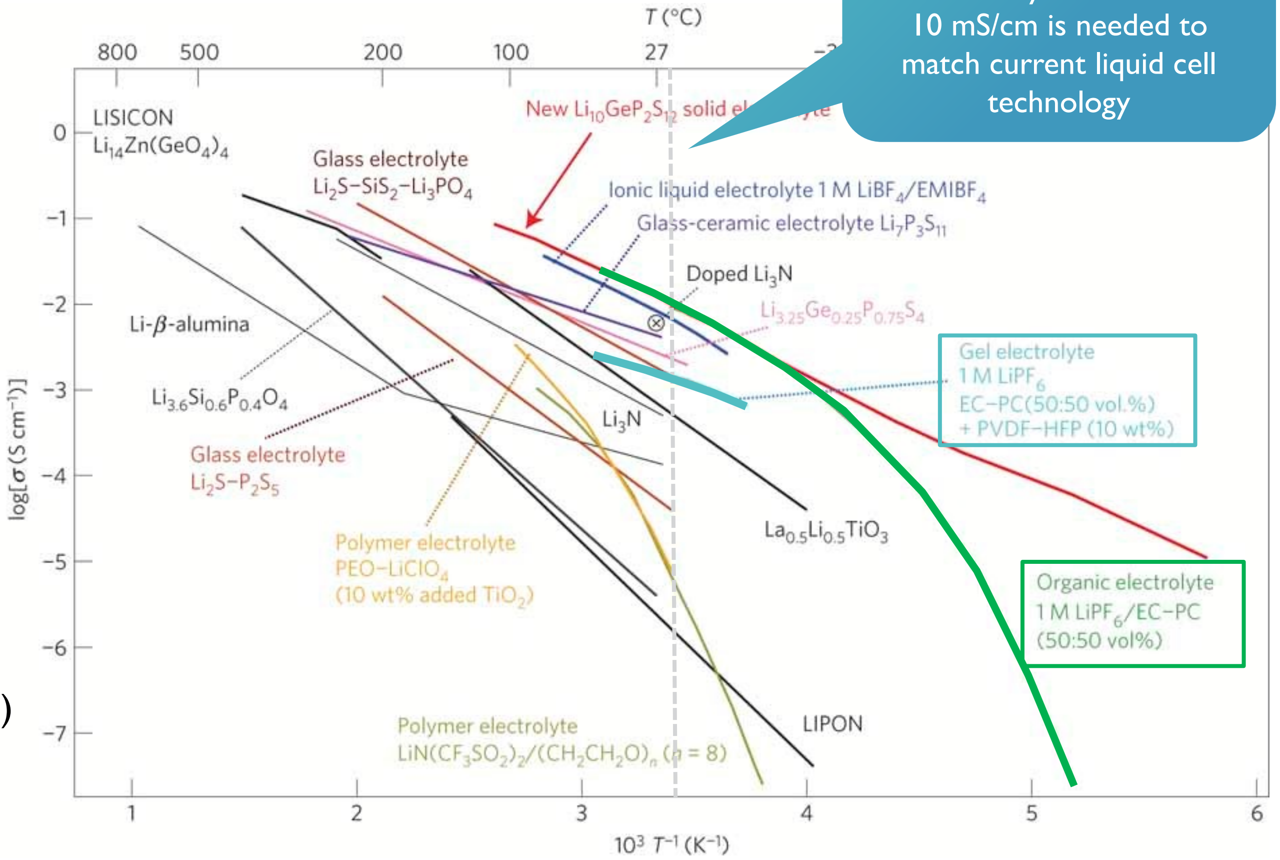


Thin-Film battery
σ >10^{-7} S/cm



MANY SOLID-STATE ELECTROLYTES OUT THERE

- Organic electrolytes (liquid)
  - *Li-salt in carbonate solvent*
  - *Li-salt in Ionic Liquid (ILE)*
- Polymer electrolyte (solid)
  - *Li-salt in PEO*
- *Polymer composite electrolyte*
  - *e.g. TiO_2 NP in PEO*
- Polymer-Gel electrolyte
  - *Polymer with added solvent*
- Inorganic crystalline SE
  - *LiSICON, LLTO, Garnet*
- Inorganic glass SE
  - *LiPON*
- Solid Composite Electrolyte (SCE)
  - *Silica and alumina with Li-salt*
  - *MOFs*



Room-temperature conductivity between 1and 10 mS/cm is needed to match current liquid cell technology

Nature Materials, DOI. 10.1038/NATMAT3066

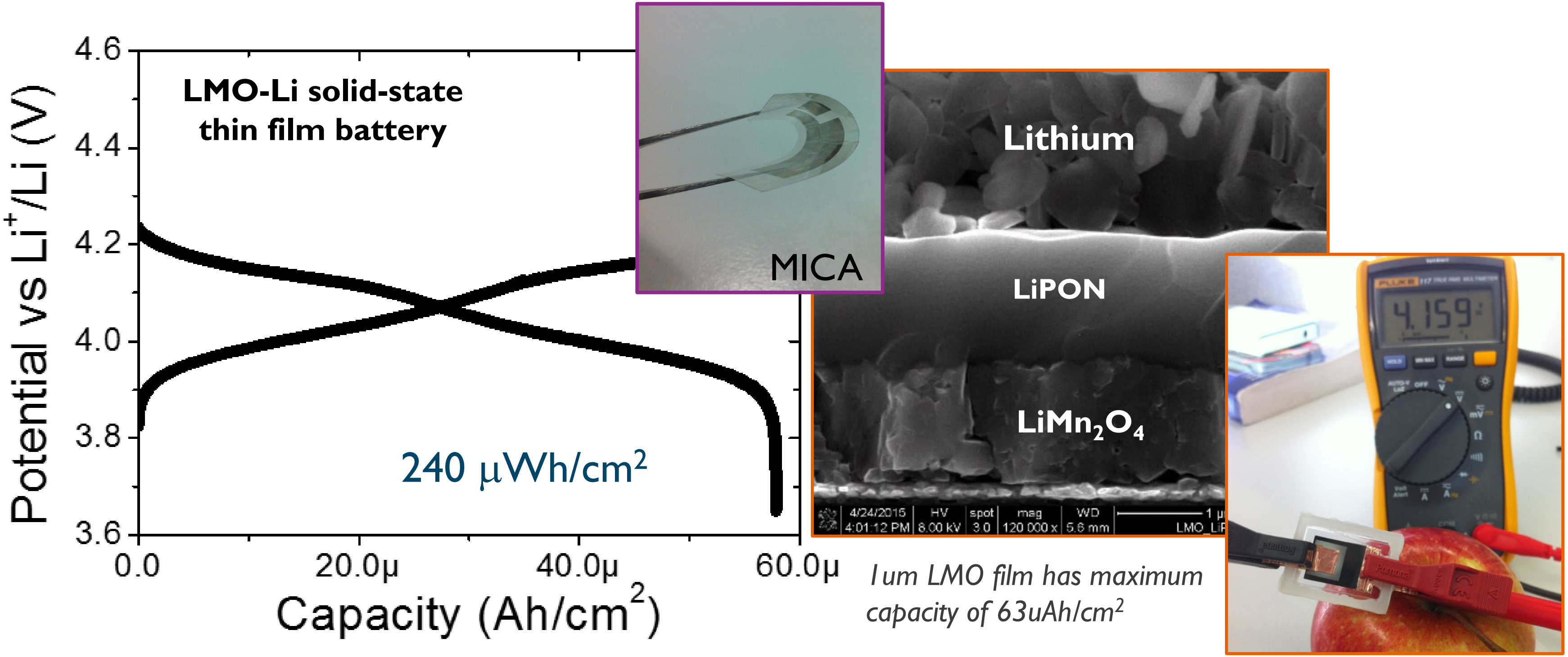
TOP-10 REQUIREMENTS FOR SOLID ELECTROLYTE COMPONENT

DIFFERENT SOLID-STATE ELECTROLYTES GIVE DIFFERENT PROPERTIES

1. *High ionic conductivity ($\sigma_i > 10^{-3}$ S/cm for large capacity batteries)*
2. *Wide electrochemical window ($0 < V$ vs. $Li^+/Li < 5.5$)*
3. *Chemical stability (temperature, against electrodes and metallic Li)*
4. *Wide temperature range (-40C ←→ 150C)*
5. *Negligible electronic conductivity ($\sigma_e < 10^{-10}$ S/cm)*
6. *Transference number for Li$^+$ close to 1 ($t_{Li^+} \approx 1$)*
7. *Resistant to lithium dendrites (mechanically –high Youngs modulus and/or chemically reaction eliminating Li dendrites)*
8. *Manufacturable (upscalable, process control)*
9. *Low toxicity (use of environmentally benign elements)*
10. *Low cost (use of abundant elements)*

LiPON WAS ONE OF THE FIRST COMMERCIAL SOLID ELECTROLYTES

HOWEVER CAN ONLY BE USED IN THIN-FILM FORMAT BECAUSE OF ITS LOW CONDUCTIVITY



1um LMO film has maximum capacity of 63uAh/cm²

The battery stack consists of a $LiMn_2O_4$ cathode layer prepared by RF-sputtering and post treatment annealed, an electrolyte layer of LiPON prepared by RF-sputtering and an anode layer consisting of a lithium metal thin film prepared by thermal evaporation.

LiPON HAS EXCELLENT CHEMICAL STABILITY BUT LOW σ_{Li}

- Organic electrolytes (liquid)
  - *Li-salt in carbonate solvent*
  - *Li-salt in Ionic Liquid (ILE)*
- Polymer electrolyte (solid)
  - *Li-salt in PEO*
- *Polymer composite electrolyte*
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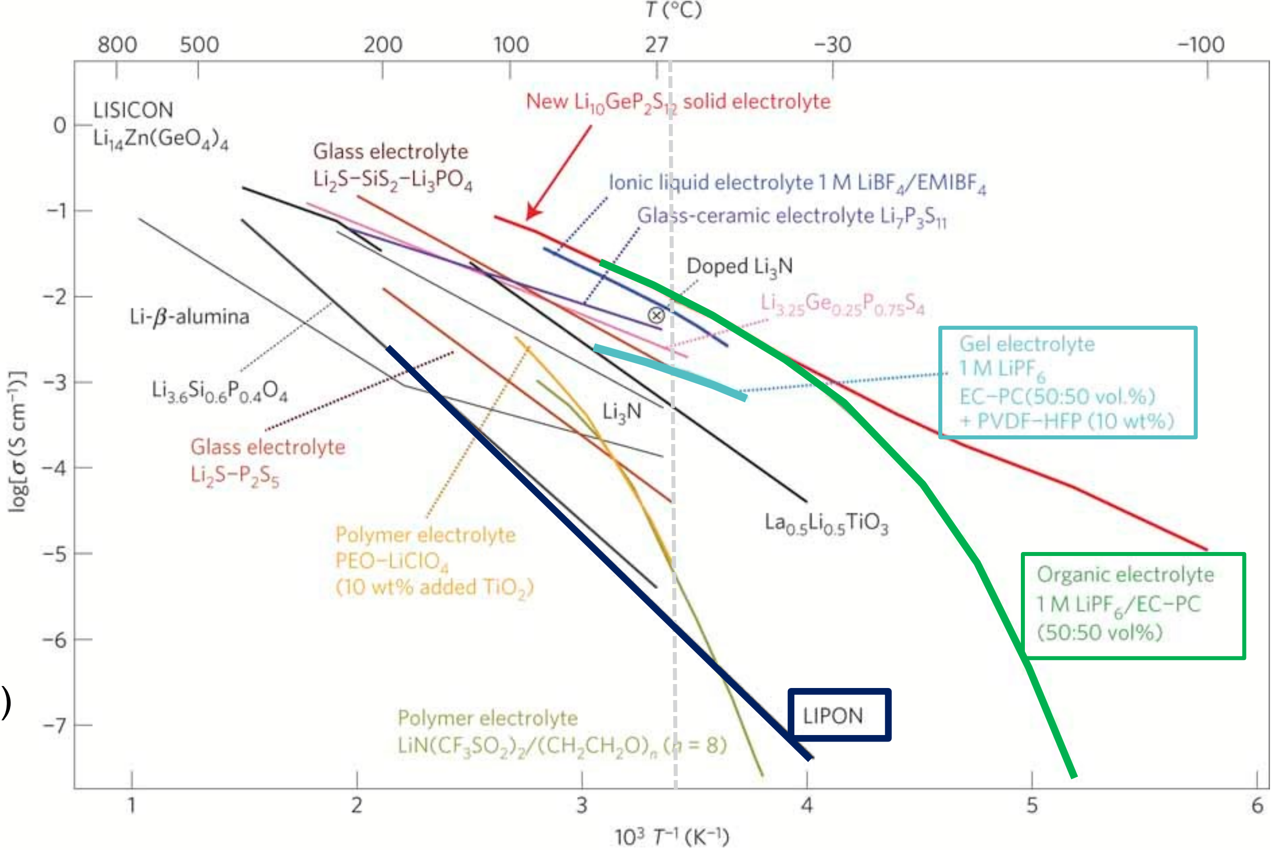
  - *Silica and alumina with Li-salt*
  - *MOFs*

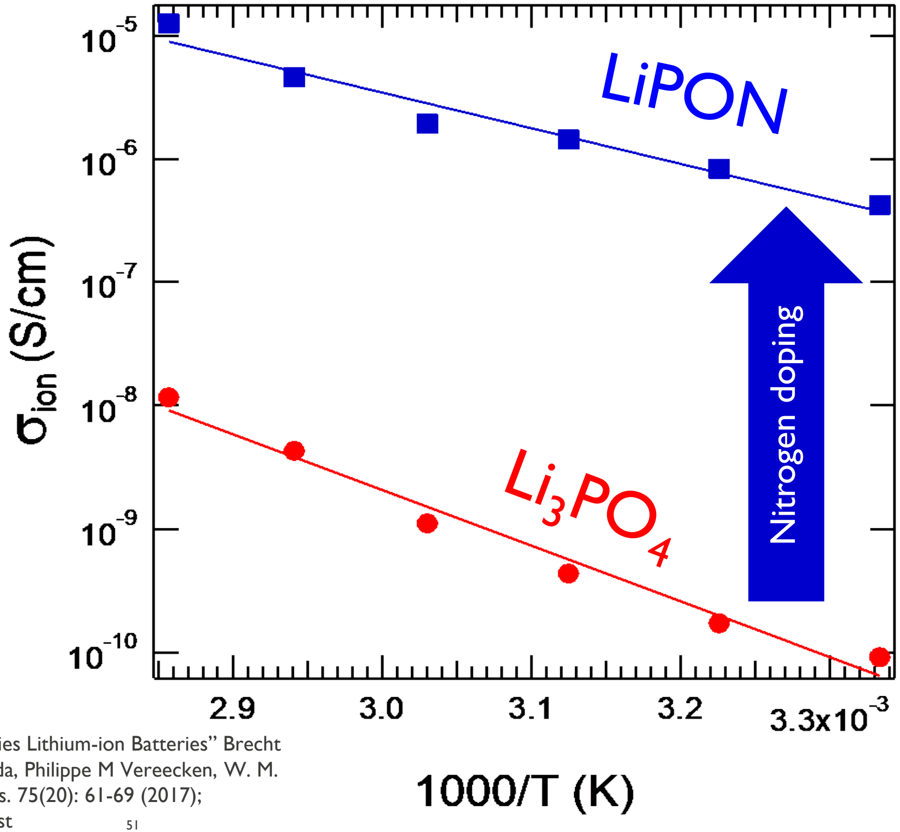


Nature Materials, DOI. 10.1038/NATMAT3066

NITROGEN-DOPED LITHIUM PHOSPHATE GLASS (LiPON)

PE-ALD LiPON films

- Doping of amorphous Li_3PO_4 with nitrogen increases enhances the Li^+ ion conductivity with 3 orders of magnitude
- Advantage of LiPON is its chemical stability against metallic lithium and broad electrochemical window of [0V ←→ ~5V]
- Unfortunately its conductivity is at least 3 orders of magnitude too low for application in large capacity batteries



"Plasma - Assisted ALD of LiPO(N) for Solid State Batteries Lithium-ion Batteries" Brecht Put, Maarten J. Mees, Norah Hornsveld, Alfonso Sepulveda, Philippe M Vereecken, W. M. M. Kessels, and Mariadriana Creatore, ECS Trans. 75(20): 61-69 (2017); doi:10.1149/07520.0061ecst

SOLID-STATE THIN-FILM BATTERIES

on 3D micro-structured substrates for
micro-storage

APPLICATION SPECTRUM

SOLID STATE Li-ION MICRO-BATTERIES

Power on board

Back-up power chip or PCB

Wireless sensor networks

distributed wireless sensors and communicators…

Wearable and Flexible

Smart carts, patches, wearables and flexible electronics…

Portable electronics

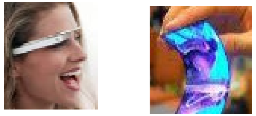
Hobby and power tools

Vehicles

Bikes, automotive, aviation, rail,…

Mobile-IT

Smart watch, phones, tablets, PC's



Renewable Energy

Home storage, micro-grid storage, grid storage

< mWh < *< Wh <* *< kWh <* *< MWh*

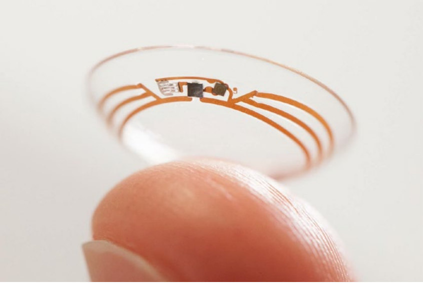
1E-04 *1E-03* *1E-02* *1E-01* *1E+00* *1E+01* *1E+02* *1E+03* *1E+04* *1E+05* *1E+06*

“TRUE” MICRO-DEVICES NEED MICRO-BATTERIES

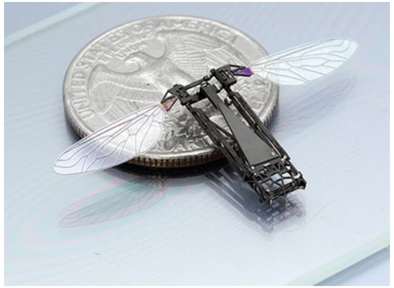
WHICH THEN URGENTLY NEED TO BE DEVELOPED

Ultimately, the smallest size of a device is limited by its battery

Digital lens



Micro drone

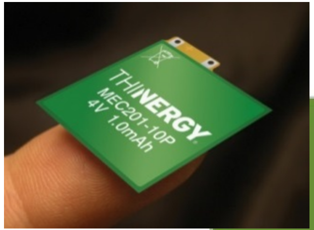


Implantable glucose sensor

Smart pill

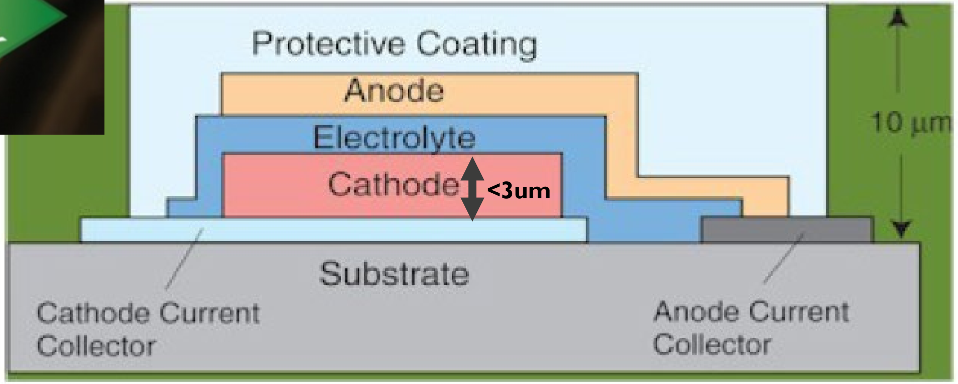
COMMERCIAL THIN-FILM BATTERIES

PLANAR GEOMETRY PROVIDES LIMITED CHARGE CAPACITY



Small cells with small capacity

(Source: John Bates, Oak Ridge Micro-Energy)



- **Thin films allow fast charging at C-rates >10C (less than 6 minutes)**
- **Charge Capacity is low (0.01 to 1 mAh) because of thin electrodes.**
- **Vacuum deposition for all layers, e.g.**
  - Cathode: $LiCoO_2$
  - Electrolyte: LiPON glass
  - Anode: Li Metal, SnN_3

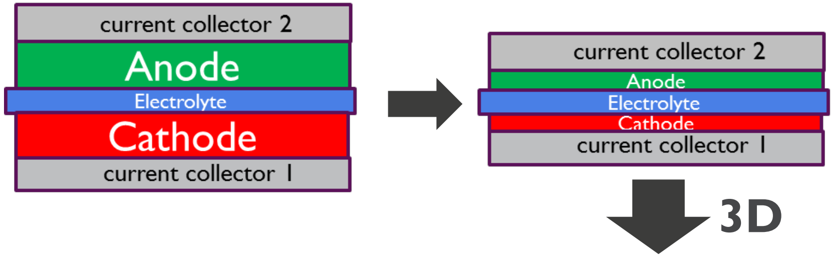
THIN-FILM BATTERIES GOING 3D

2D (Planar)

Capacity is increased by increasing film thickness but also slows down the charging (practical limit around 5um thickness)

Higher capacity
Slower charging

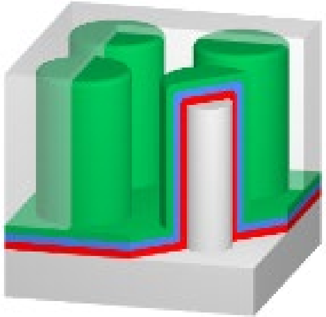
Lower capacity
Faster charging



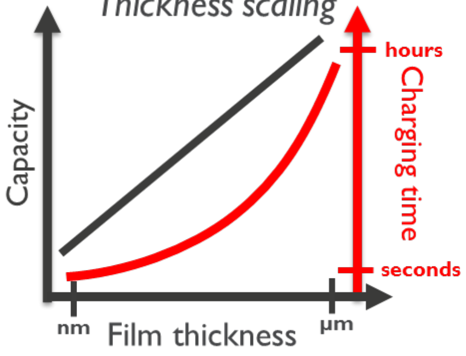
High capacity
Fast charging

3D (Microstructured)

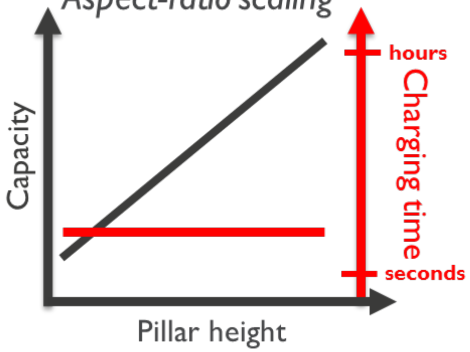
Capacity is increased by increasing the effective surface area, while the films can be kept thin for fast charge/discharge kinetics



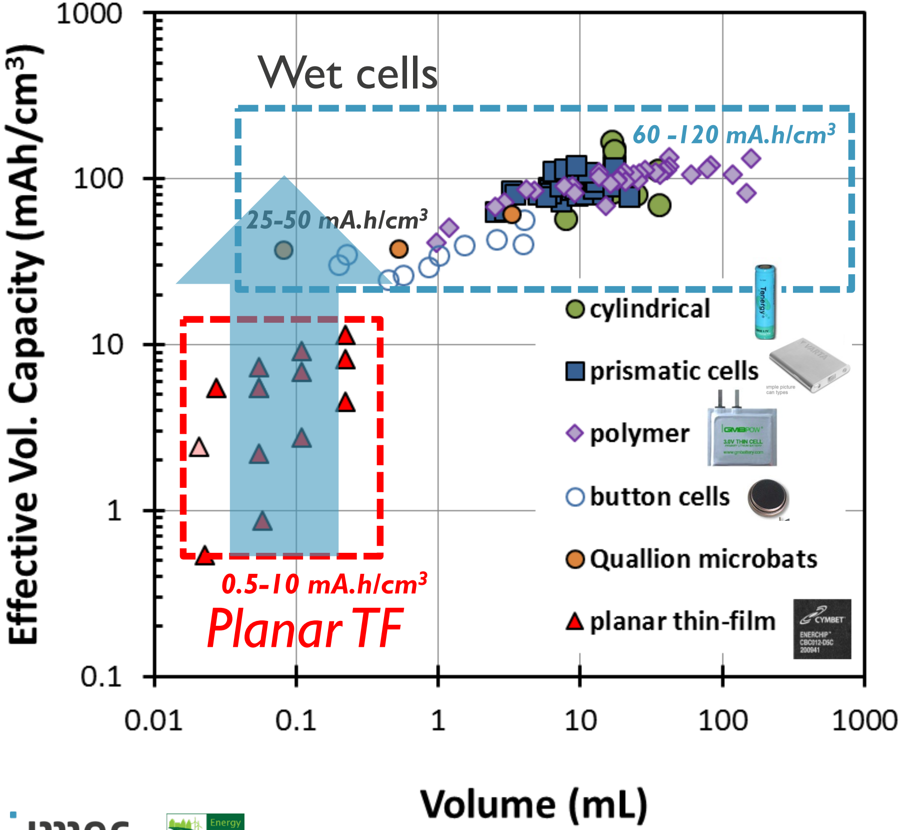
“Thickness scaling”



“Aspect-ratio scaling”



3D THIN-FILM BATTERY FOR HIGH-SPEED MICRO STORAGE

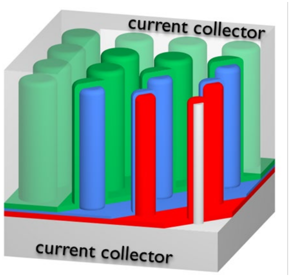


Requirements for micro storage

- ***Ultra small form factor:*** ≤ 1 mL
- ***High volumetric capacity:*** 60 -120 mAh/cm^3
- ***Fast charging:*** 80% max. capacity in 3 min charging (20C)
- ***Safety & Stability***

Our solution:

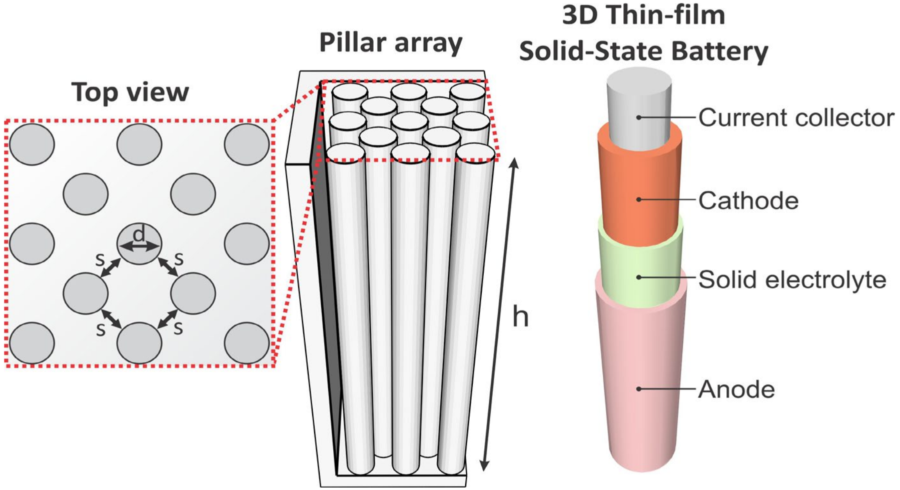
<u>3D Solid-State Thin-Film Batteries</u>

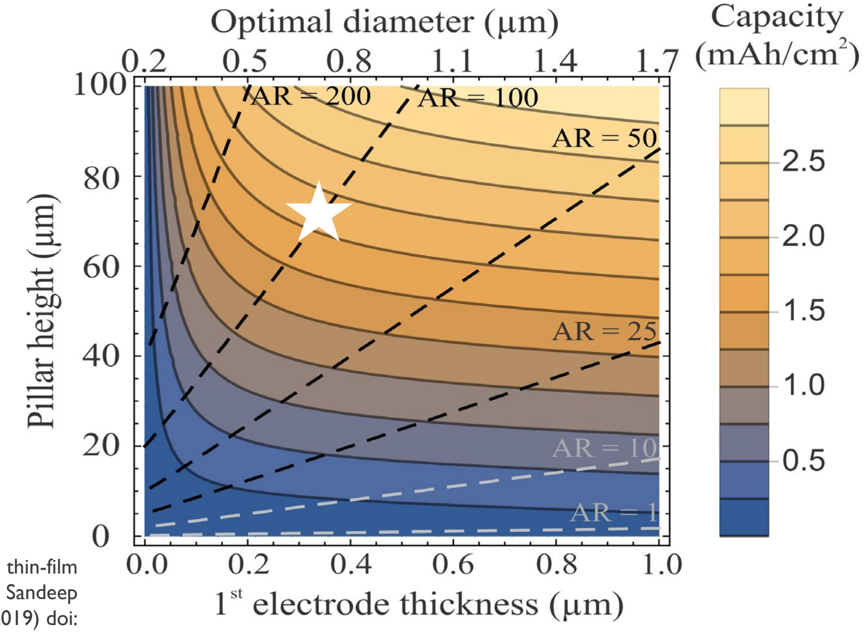


FOOTPRINT CAPACITY > $2mAh/cm^2$

CAPACITY DENSITY >$100mAh/cm^3$

- The 3D thin-film battery could easily match the capacity and energy density of commercial wet cells, but it should be at much higher C-rates (>10C)

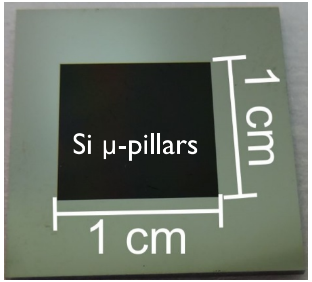


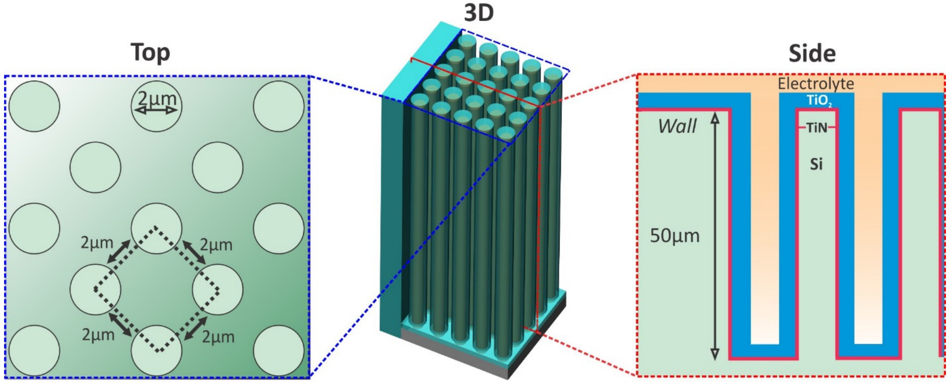


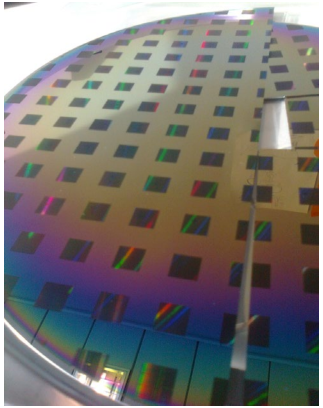
"Towards 3D Thin-Film Batteries: Optimal current-collector design and scalable fabrication of TiO2 thin-film electrodes" Sébastien Moitzheim, Joan Elisabeth Balder, Riina Ritasalo, Satu Ek, Paul Poodt, Sandeep Unnikrishnan, Stefan De Gendt, Philippe M. Vereecken, ACS Appl. Energy Mater. **2**, 3, 1774-1783 (2019) doi: 10.1021/acsaem.8b01905

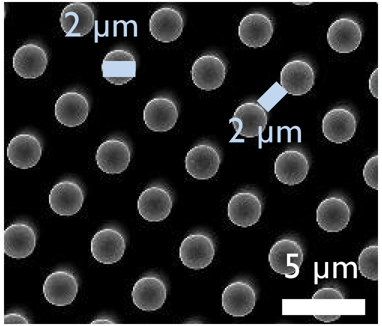
Our silicon pillar arrays for micro-structured current collector substrates

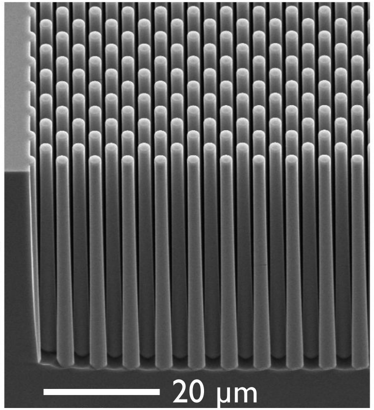
Si µ-pillars are fabricated by lithography patterning and deep reactive ion etching on 300 mm Si wafers







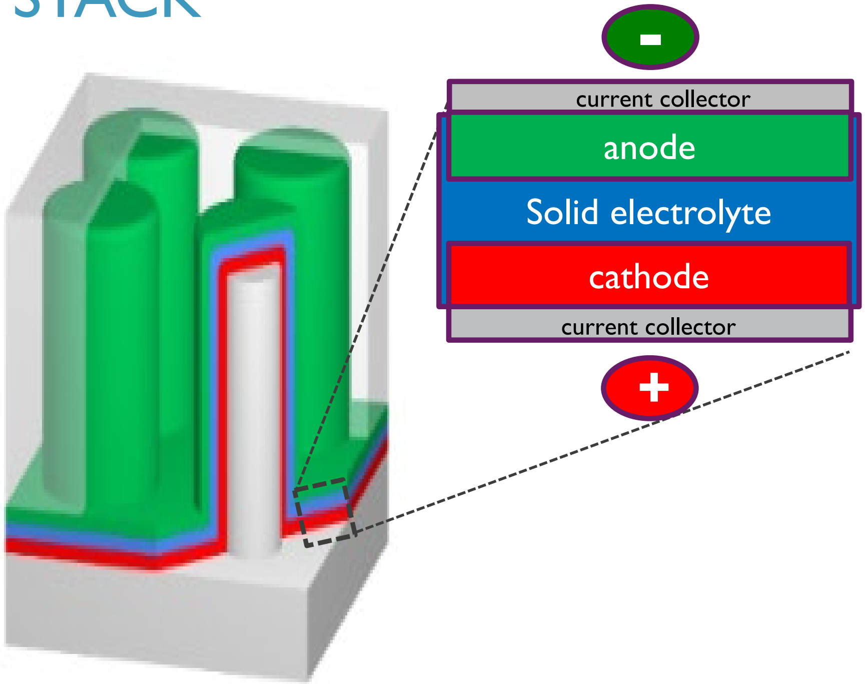


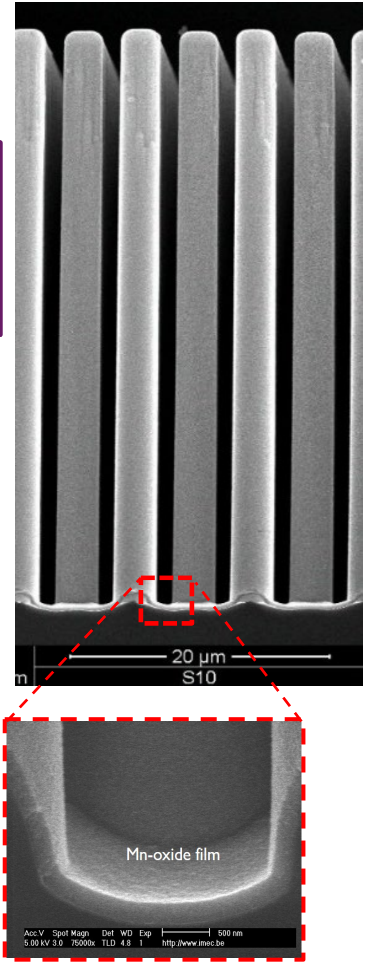


- **pillar diameter:** 2 µm
- **Inter-pillar spacing:** 2 µm
- **Pillar height: 50-60µm**

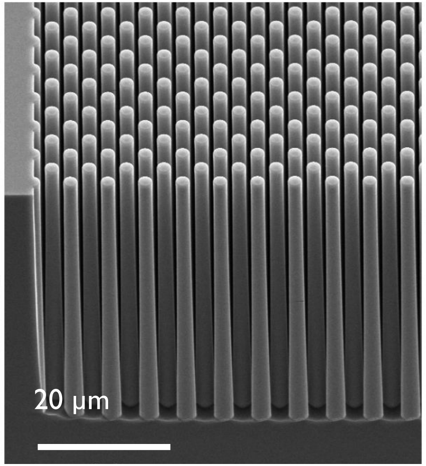
Area enhancement of 20-25x

OUR 3D THIN-FILM STACK





Area enhancement of 25x

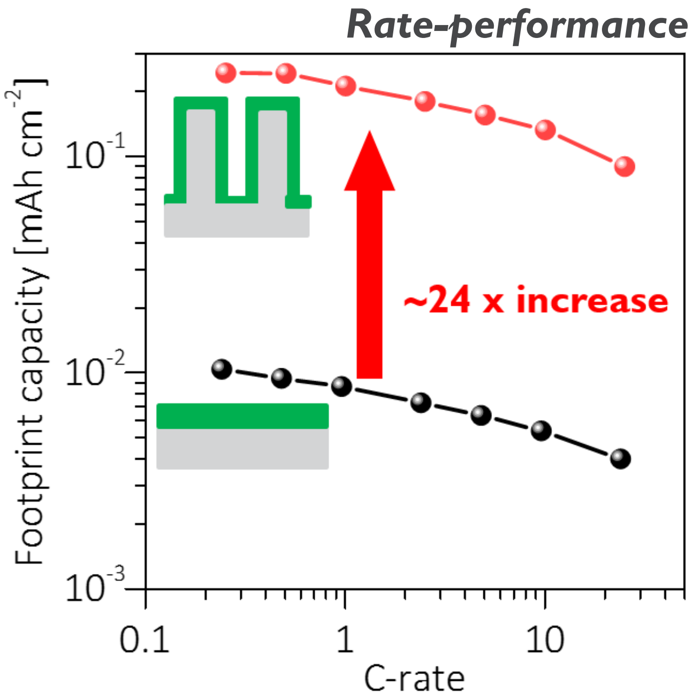


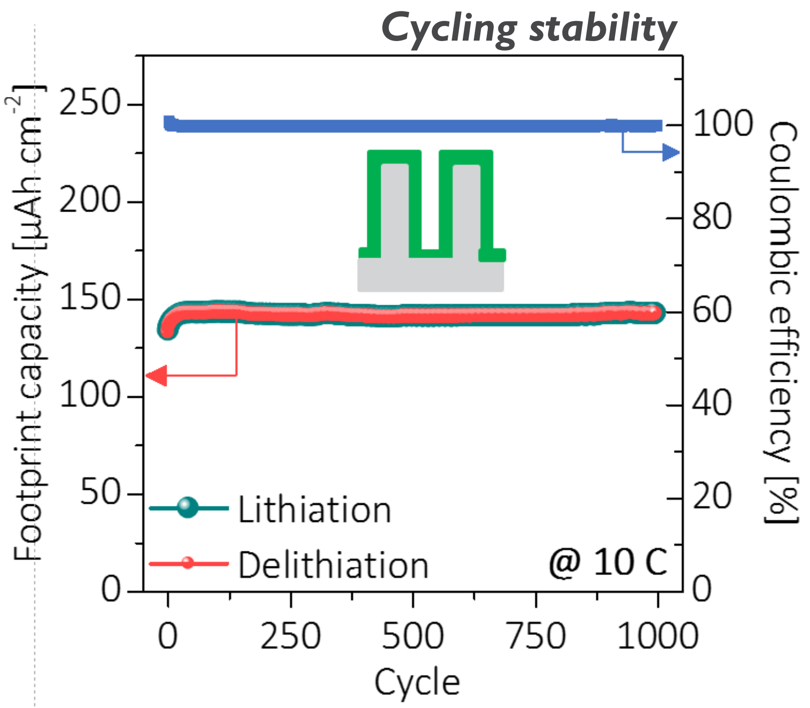
- **Conformal coatings of cathode, anode and electrolyte thin-films**
- **Low temperature budget**
- **Industrially scalable techniques**

" Chlorine Doping of Amorphous TiO2 for Increased Capacity and Faster Li+-Ion Storage"
S. Moitzheim, J.E. Balder, P. Poodt, S. Unnikrishnan S. De Gendt and P.M. Vereecken,
Chem. Mater., **29**, 23, 10007–10018 (2017) DOI: 10.1021/acs.chemmater.7b03478

PRINCIPLE WORKS

PERFORMANCE OF OUR 3D Cl-doped TiO_2 THIN-FILM ELECTRODE



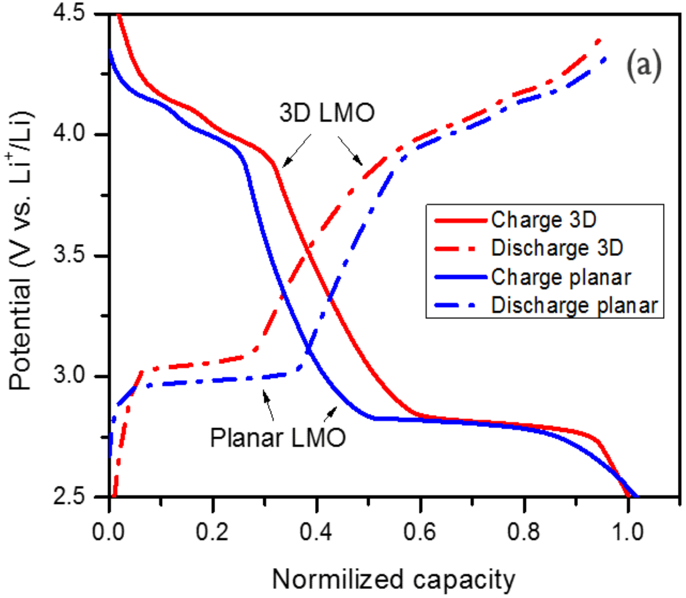


Same rate performance for 3D and planar electrodes but with 24 times higher capacity for the 3D TiO_2 electrode

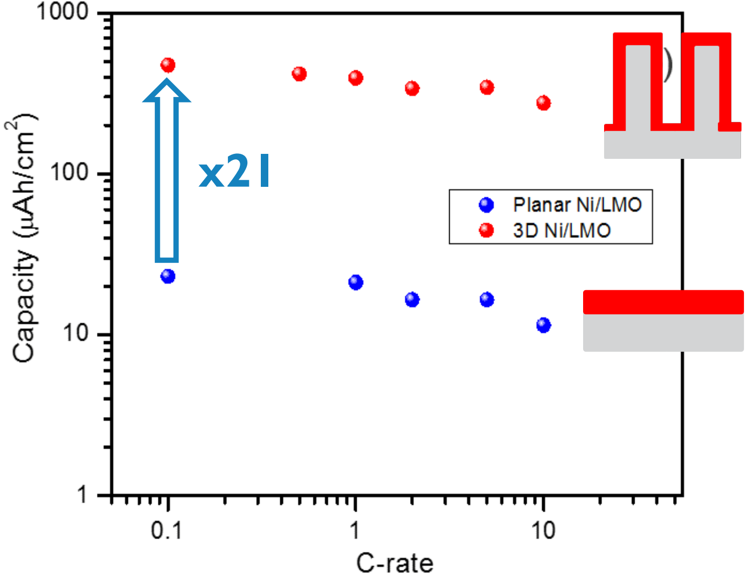
PRINCIPLE WORKS

PERFORMANCE OF OUR 3D $LiMn_2O_4$ THIN-FILM ELECTRODE

- First demonstration of a 3D LMO electrode



Rate-performance

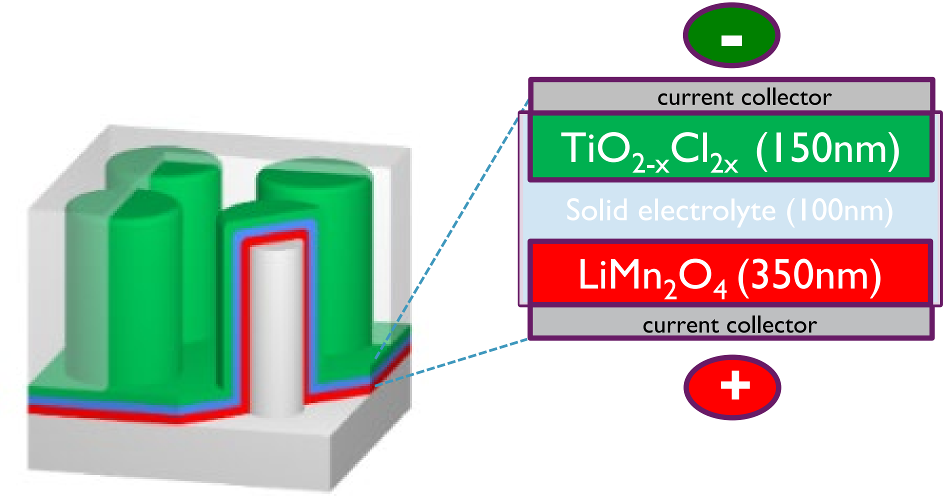


Same rate performance for 3D and planar electrodes but with 21 times higher capacity for the 3D LMO electrode

3D THIN-FILM ELECTRODES STATUS

LMO AND DOPED TITANIA HALF CELLS PLOTTED TOGETHER

Double the capacity of best planar thin-film battery and with ~60mA/cm^3 already better than coin cells



-

current collector

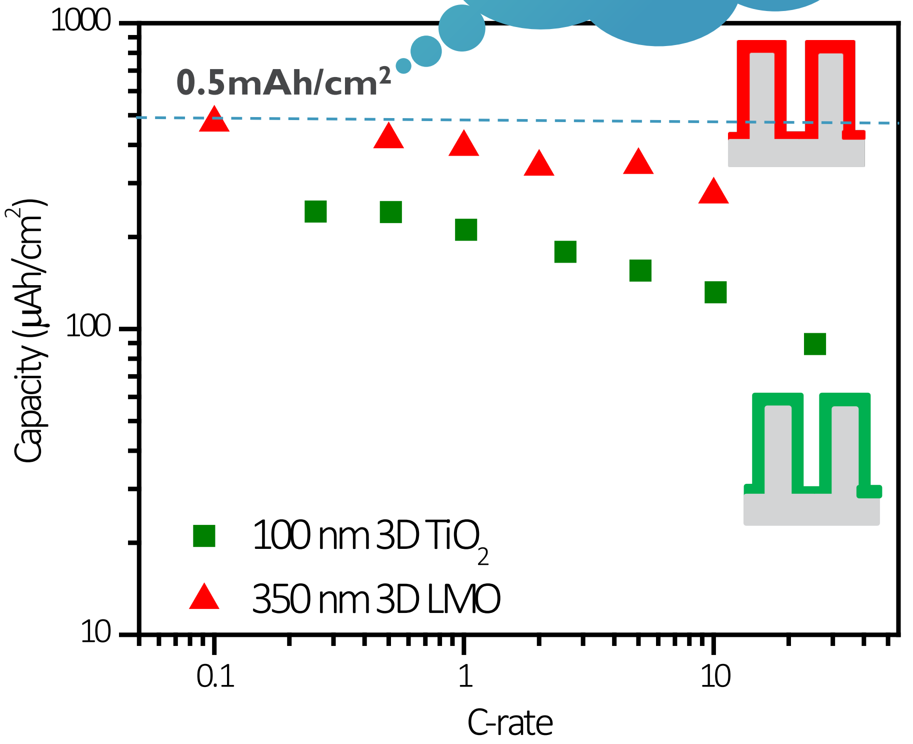
$TiO_{2-x}Cl_{2x}$ (150nm)

Solid electrolyte (100nm)

$LiMn_2O_4$ (350nm)

current collector

+

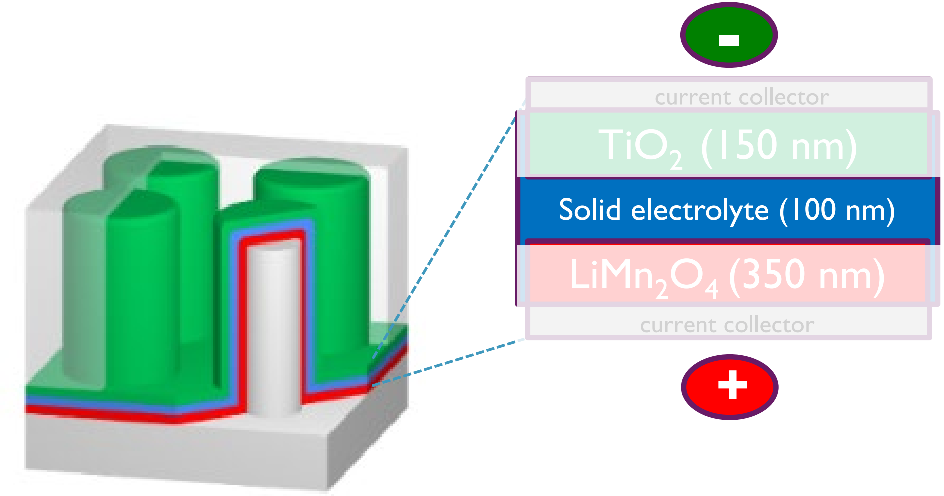


- Capacity and rate-performance of 3D thin-film cathode and anode will match in the final device*

*Outer electrode will have large volume for same thickness

THIN-FILM ELECTROLYTE

CONFORMAL ELECTROLYTE IS THE BOTTLE NECK IN THE INTEGRATION

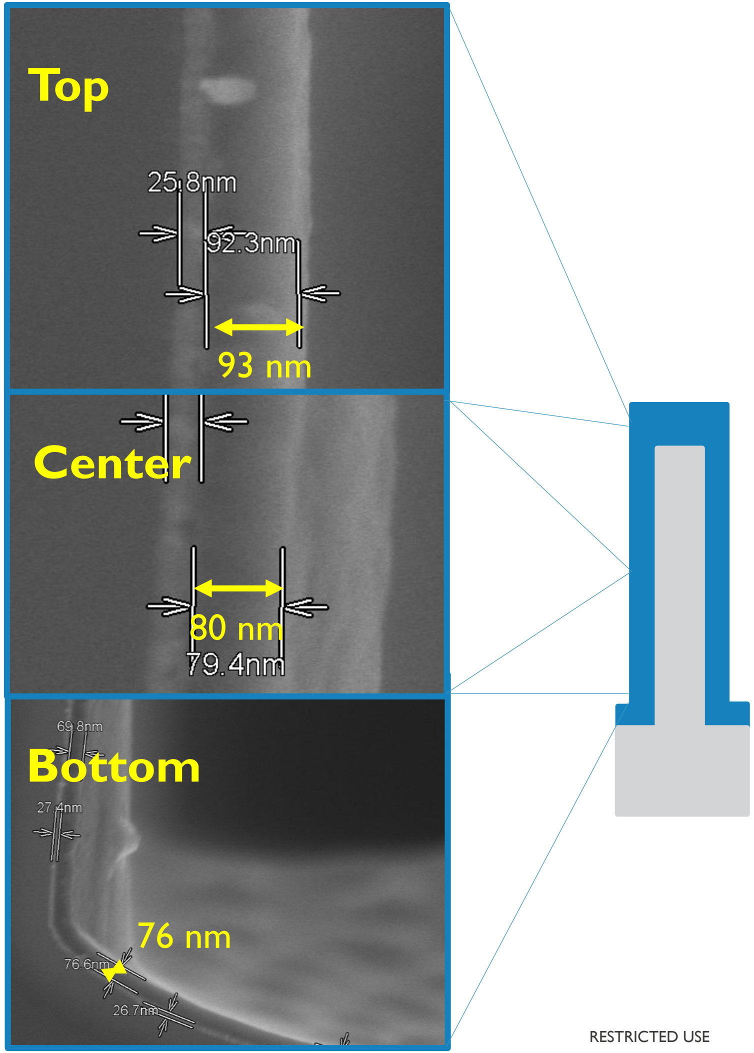


We are working on two approaches for conformal thin-film electrolyte:

- Conformal LiPON thin-films
- Conformal Solid nano-Composite Electrolyte (nano-SCE) thin-films
- Currently, we are working on the integration of the electrolyte in the stack

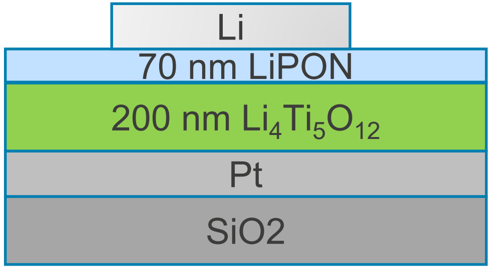
LiPON THIN-FILM ELECTROLYTE

- Conformal LiPON thin-films were successfully deposited by plasma-enhanced atomic layer deposition (PEALD)
  - ~ 80% step coverage was achieved
- The LiPON thin-films (planar!) have an ionic conductivity of **5x10^{-7} S/cm** at 300K
- First to demonstrate a planar thin-film battery with ALD LiPON
- Next, a full 3D cell will be built



"Plasma-assisted ALD of LiPO(N) for Solid State Batteries" Brecht Put, Maarten J. Mees, Norah Hornsveld, Alfonso Sepulveda, Philippe M Vereecken, W. M. M. Kessels and Mariadriana Creatore, J. Electrochem. Soc. **166**, 6, A1239-A1242 (2019) doi: 10.1149/2.1191906jes

PLANAR THIN-FILM BATTERY WITH ALD LiPON



Li

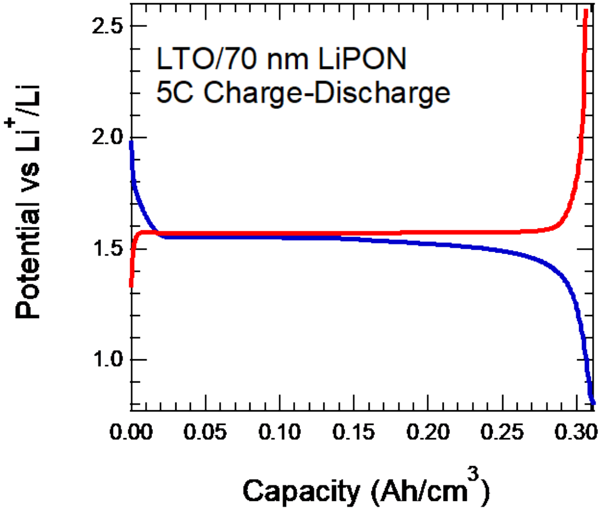
70 nm LiPON

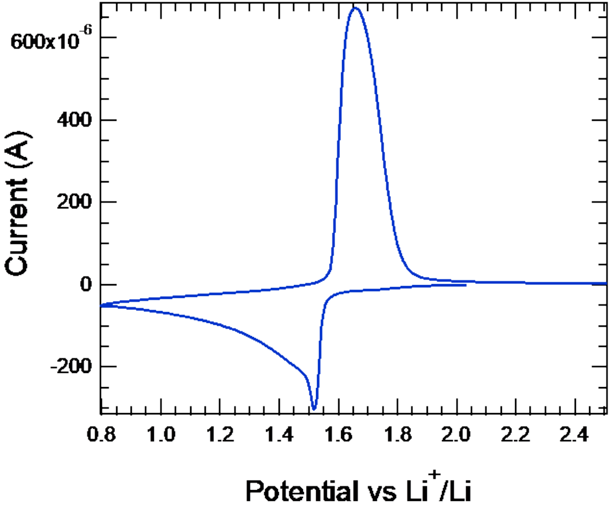
200 nm $Li_4Ti_5O_{12}$

Pt

SiO2

- **First battery employing ultra thin ALD LIPON**
  - **R = 15 Ω.cm²**
- **Reaches 87 mAh/g**
- **Li metal in contact with 70 nm LiPON is stable**





"Plasma-assisted ALD of LiPO(N) for Solid State Batteries" Brecht Put, Maarten J. Mees, Norah Hornsveld, Alfonso Sepulveda, Philippe M Vereecken, W. M. M. Kessels and Mariadriana Creatore, J. Electrochem. Soc. **166**, 6, A1239-A1242 (2019) doi: 10.1149/2.1191906jes

100 nm THIN-FILM POLYMER-SCE

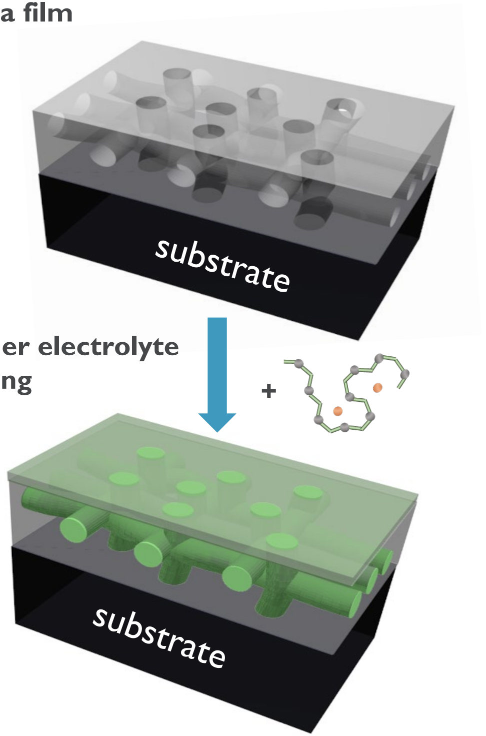
○ Two-step deposition for SCE

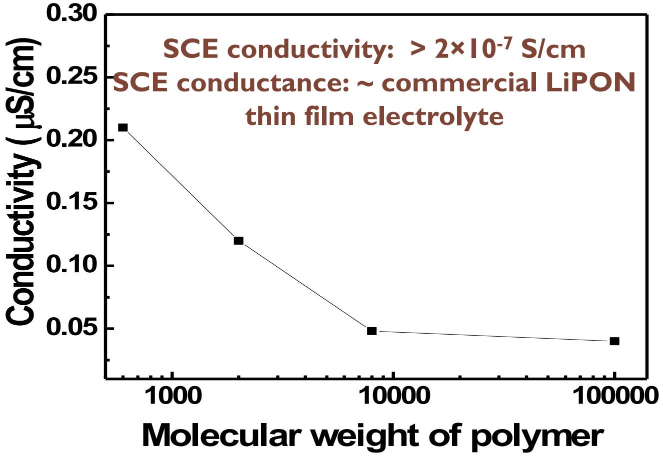
- **Deposit porous silica film**

100 nm thick
mesoporous
silica film

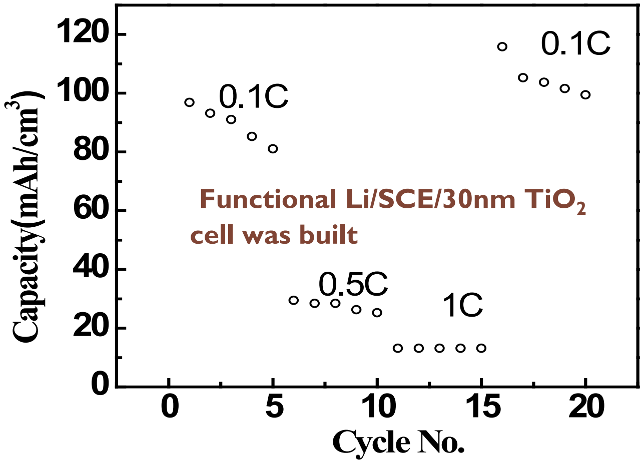
- **Fill pores with polymer electrolyte by spin coating**

polymer-SCE
thin film





SCE conductivity: > 2×10^{-7} S/cm
SCE conductance: ~ commercial LiPON thin film electrolyte

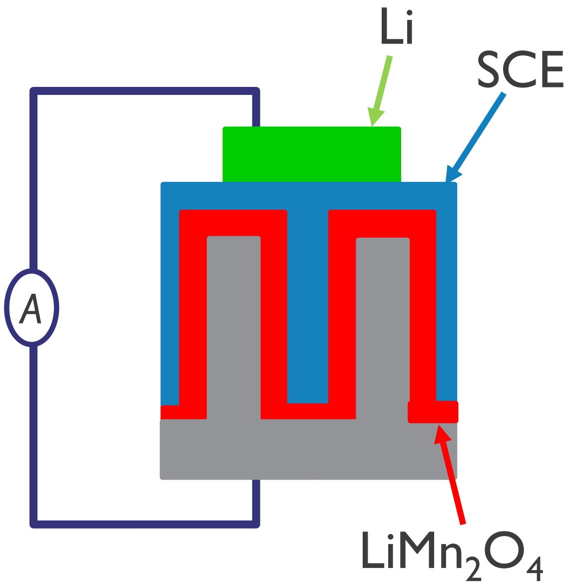


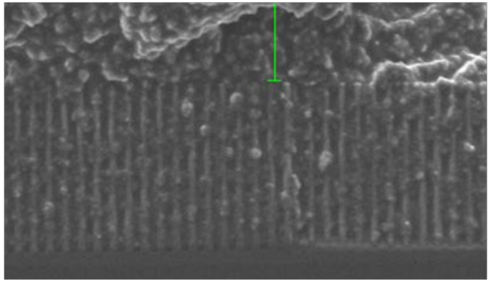
Functional Li/SCE/30nm TiO_2 cell was built

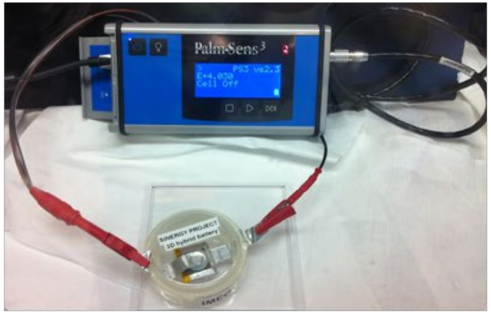
"100 nm Thin-Film Solid-Composite Electrolyte for Lithium ion batteries" Xubin Chen and Philippe M. Vereecken, *Adv. Mater. Interfaces* **4** (4), 1600877 (2017). DOI:10.1002/admi.201600877
Xubin Chen, Solid Composite Electrolytes for Lithium Ion Batteries", Ph.D dissertation, June 2018.

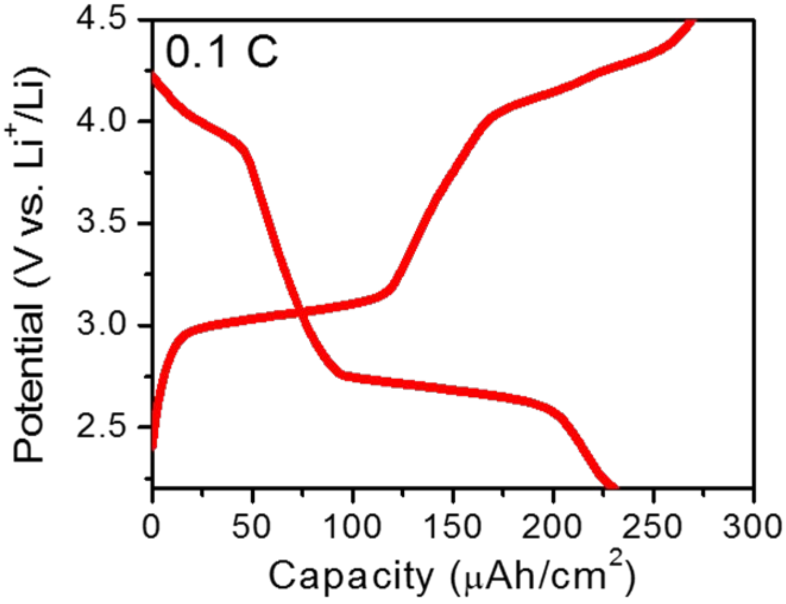
3D-PLANAR HYBRID Li-ION BATTERY

In anticipation of the conformal electrolyte, a functional solid-state Li-ion battery was demonstrated using our 3D LMO cathode versus a Li-foil using one of our nanocomposite solid electrolytes (SCE) which is casted from a liquid precursor









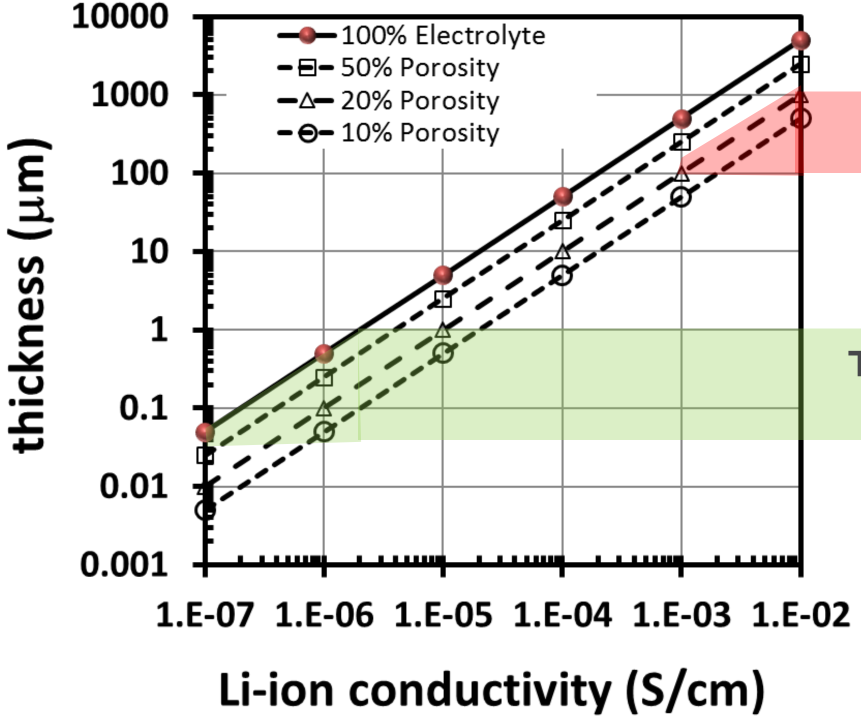
0.25mA/cm^2 with 30% capacity at 5C

NOW BACK TO THE *LARGE CAPACITY SOLID-STATE CELLS*

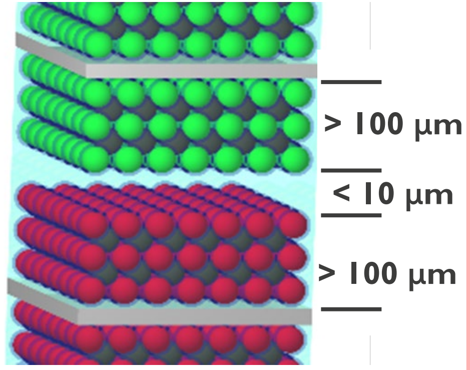
CONDUCTIVITY OF ELECTROLYTE DETERMINES ITS THICKNESS

AND THUS THE POSSIBLE CELL ARCHITECTURE

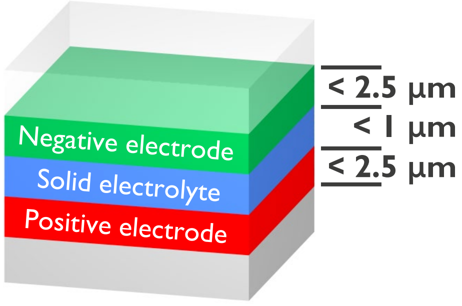
For an maximum internal cell resistance of 50Ω.cm²



Powder battery
$\sigma > 10^{-3}$ S/cm

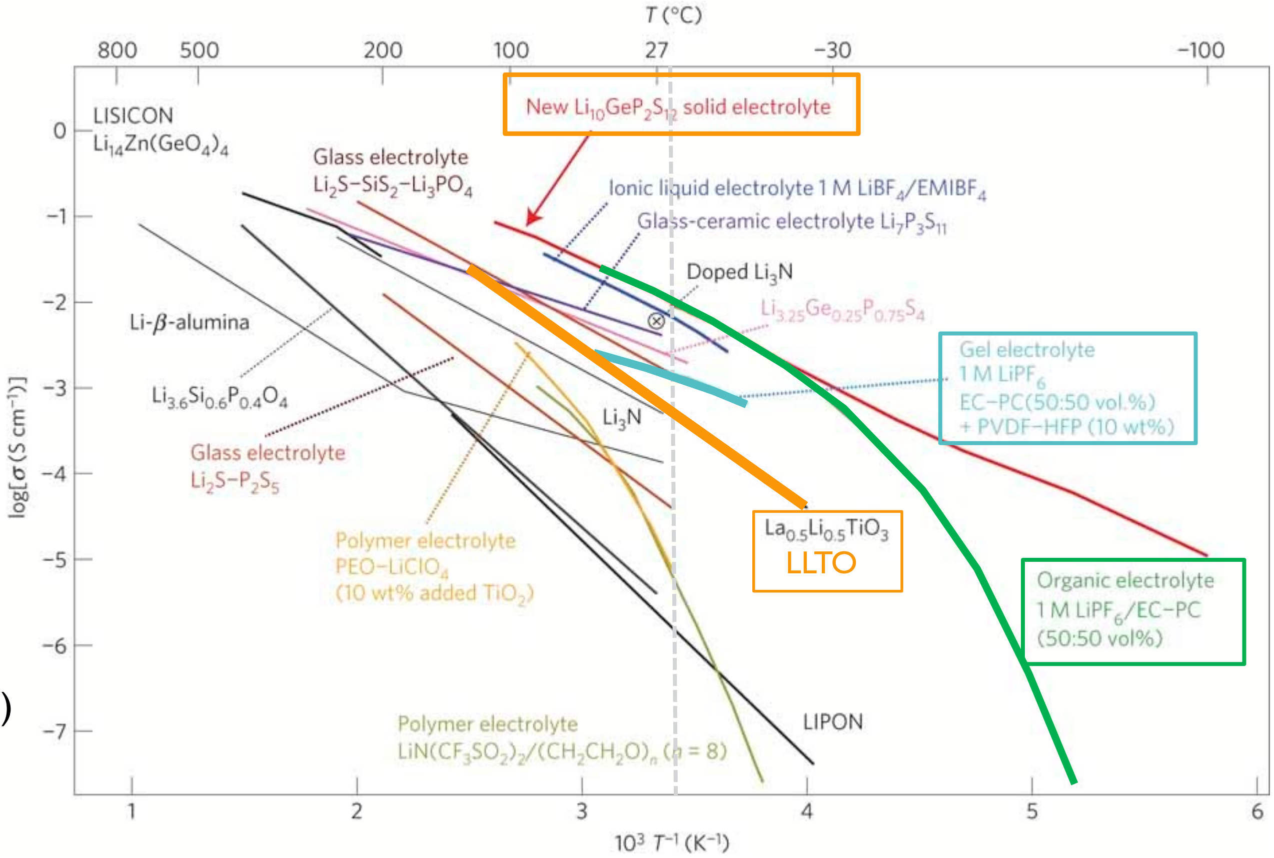


Thin-Film battery
$\sigma > 10^{-7}$ S/cm



OXIDIC SOLID ELECTROLYTES WITH ION CONDUCTIVITY <1 mS/cm

- Organic electrolytes (liquid)
  - *Li-salt in carbonate solvent*
  - *Li-salt in Ionic Liquid (ILE)*
- Polymer electrolyte (solid)
  - *Li-salt in PEO*
- *Polymer composite electrolyte*
  - *e.g. TiO$_2$ NP in PEO*
- Polymer-Gel electrolyte
  - *Polymer with added solvent*
- Inorganic crystalline SE
  - *Perovskite, Garnet, LiSICON,*
- Inorganic glass SE
  - *LiPON*
- Solid Composite Electrolyte (SCE)
  - *Silica and alumina with Li-salt*
  - *MOFs*

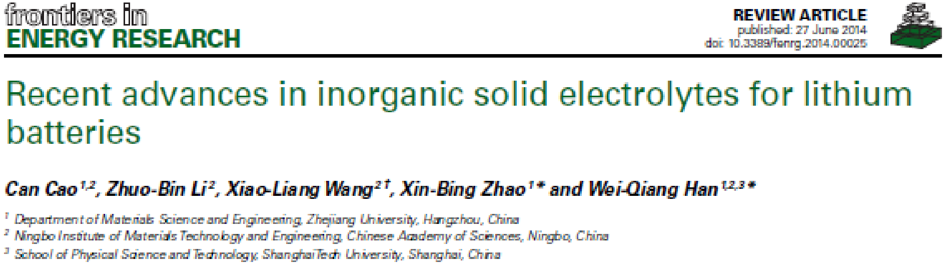


Nature Materials, DOI. 10.1038/NATMAT3066

PEROVSKITE – $Li_{0.5}La_{0.5}TiO_3$ OR LLTO

RECORDHOLDER FOR MANY YEARS WITH RT ION CONDUCTIVITY ~1mS/cm

- Li-ions can move through channels in the crystal to leave or occupy Li-sites similarly as it is the case in electrode materials
- However, small EC window as it is unstable below 1.5V vs. Li^+/Li



frontiers in
ENERGY RESEARCH

REVIEW ARTICLE
published: 27 June 2014
doi: 10.3389/fenrg.2014.00025

Recent advances in inorganic solid electrolytes for lithium batteries

Can Cao[1,2], *Zhuo-Bin Li*[2], *Xiao-Liang Wang*[2†], *Xin-Bing Zhao*[1*] *and Wei-Qiang Han*[1,2,3*]

[1] Department of Materials Science and Engineering, Zhejiang University, Hangzhou, China
[2] Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, China
[3] School of Physical Science and Technology, ShanghaiTech University, Shanghai, China

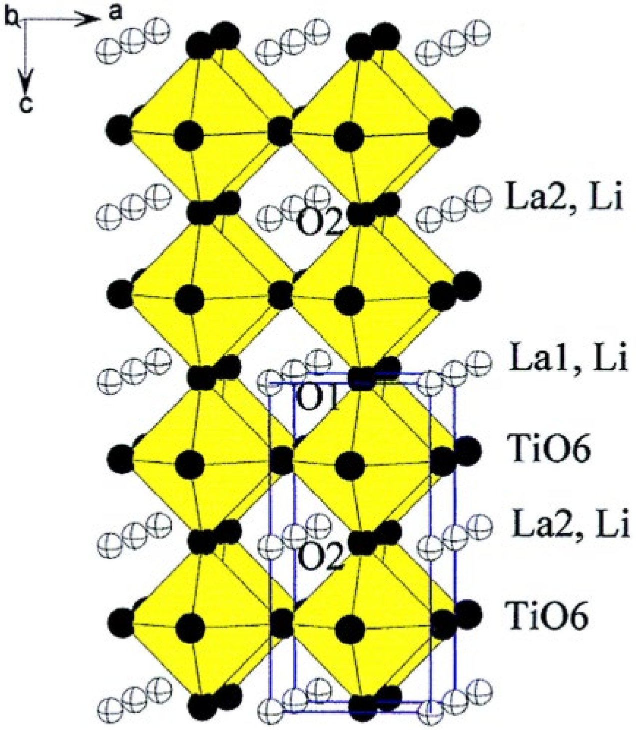
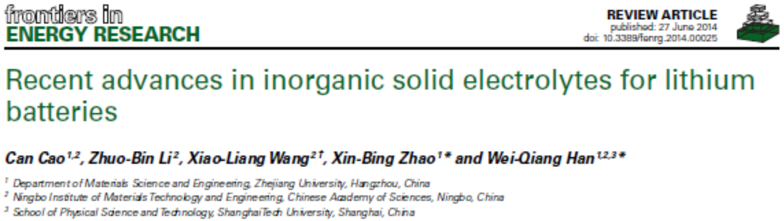


FIGURE 8 | Crystal structure of tetragonal LLTO. Reproduced with permission of Stramare et al. (2003).

GARNET – $Li_7La_3Zr_4O_{12}$ OR LLZO

RT ION CONDUCTIVITY BETWEEN 0.1-1mS/cm FOR CUBIC STRUCTURE

- High conductivity cubic structure can be stabilized by doping with substitution of La and Zr
- Large EC window and stable against metallic lithium



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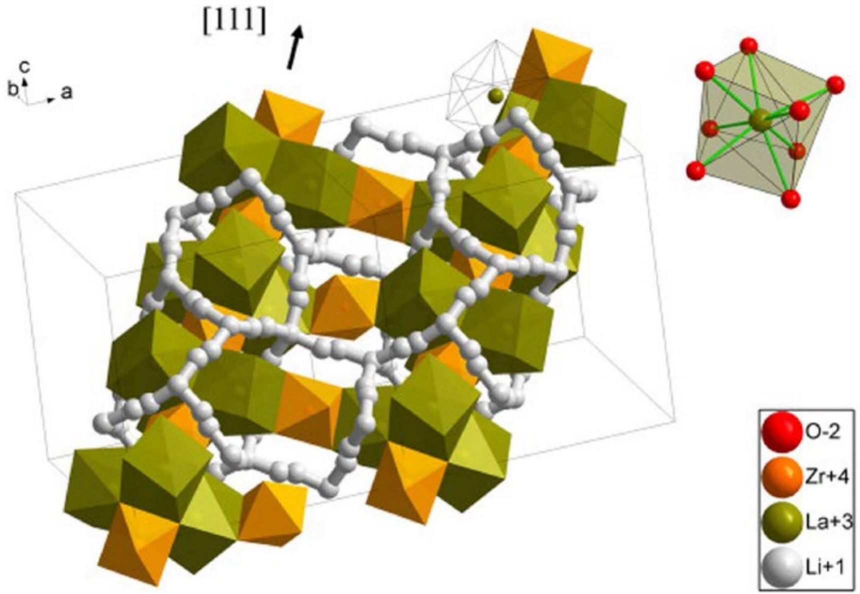
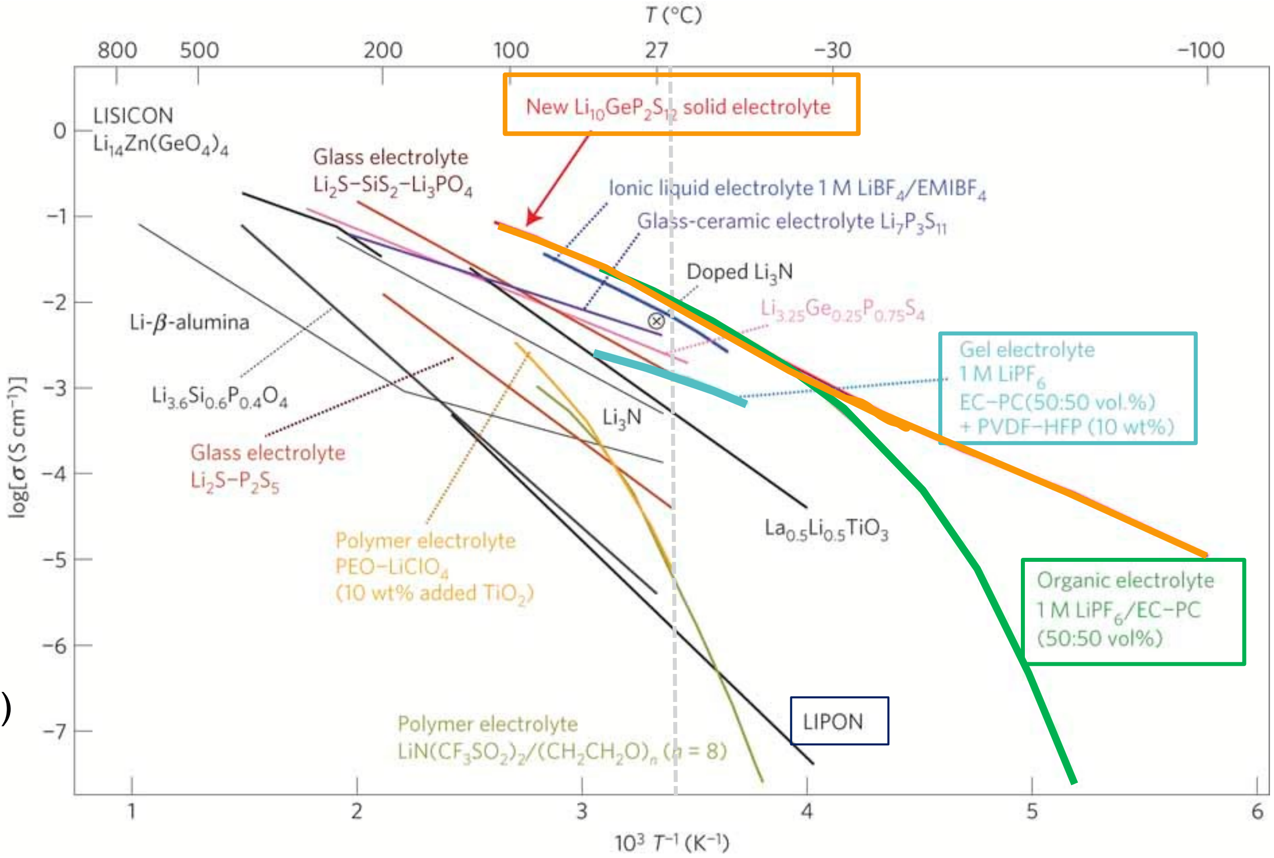


FIGURE 6 | Crystallographic structure of cubic LLZO. Reproduced with permission of Dumon et al. (2013).

SULFIDIC SOLID ELECTROLYTES WITH ION CONDUCTIVITY >10 mS/cm

- Organic electrolytes (liquid)
  - *Li-salt in carbonate solvent*
  - *Li-salt in Ionic Liquid (ILE)*
- Polymer electrolyte (solid)
  - *Li-salt in PEO*
- *Polymer composite electrolyte*
  - *e.g.* TiO_2 *NP in PEO*
- Polymer-Gel electrolyte
  - *Polymer with added solvent*
- Inorganic crystalline SE
  - *LiSICON, LLTO, Garnet*
- Inorganic glass SE
  - *LiPON*
- Solid Composite Electrolyte (SCE)
  - *Silica and alumina with Li-salt*
  - *MOFs*

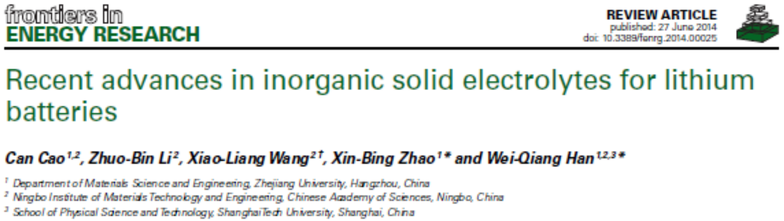


Nature Materials, DOI. 10.1038/NATMAT3066

THIO-LISICON AS NEW FAMILY OF SUPERIONIC CONDUCTORS

$Li_{10}GeP_2S_{12}$ WITH RT ION CONDUCTIVITY OF ~10 mS/cm

- S is larger than O and thio-LiSICON have more open crystal structure than oxidic LiSICON
- 3D framework with Li diffusion in a, b, and c directions
- Large EC window though some stability issues are remaining



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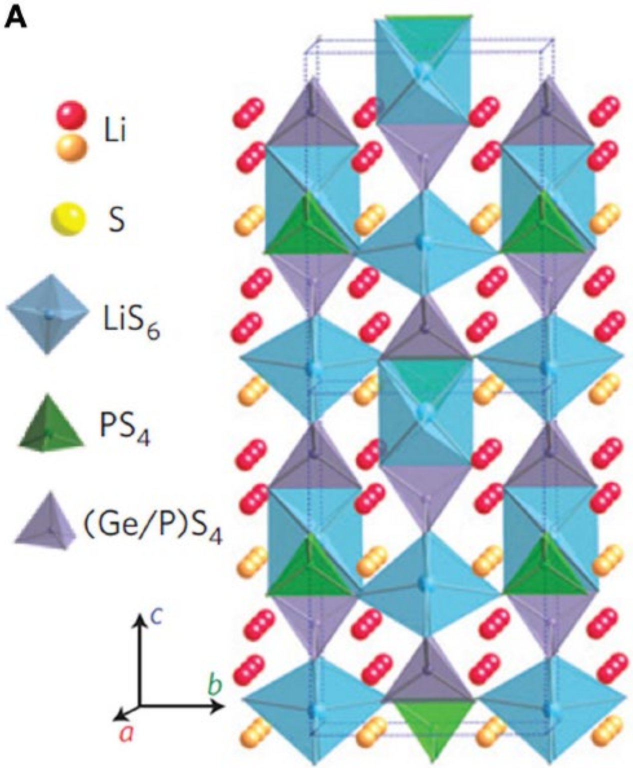
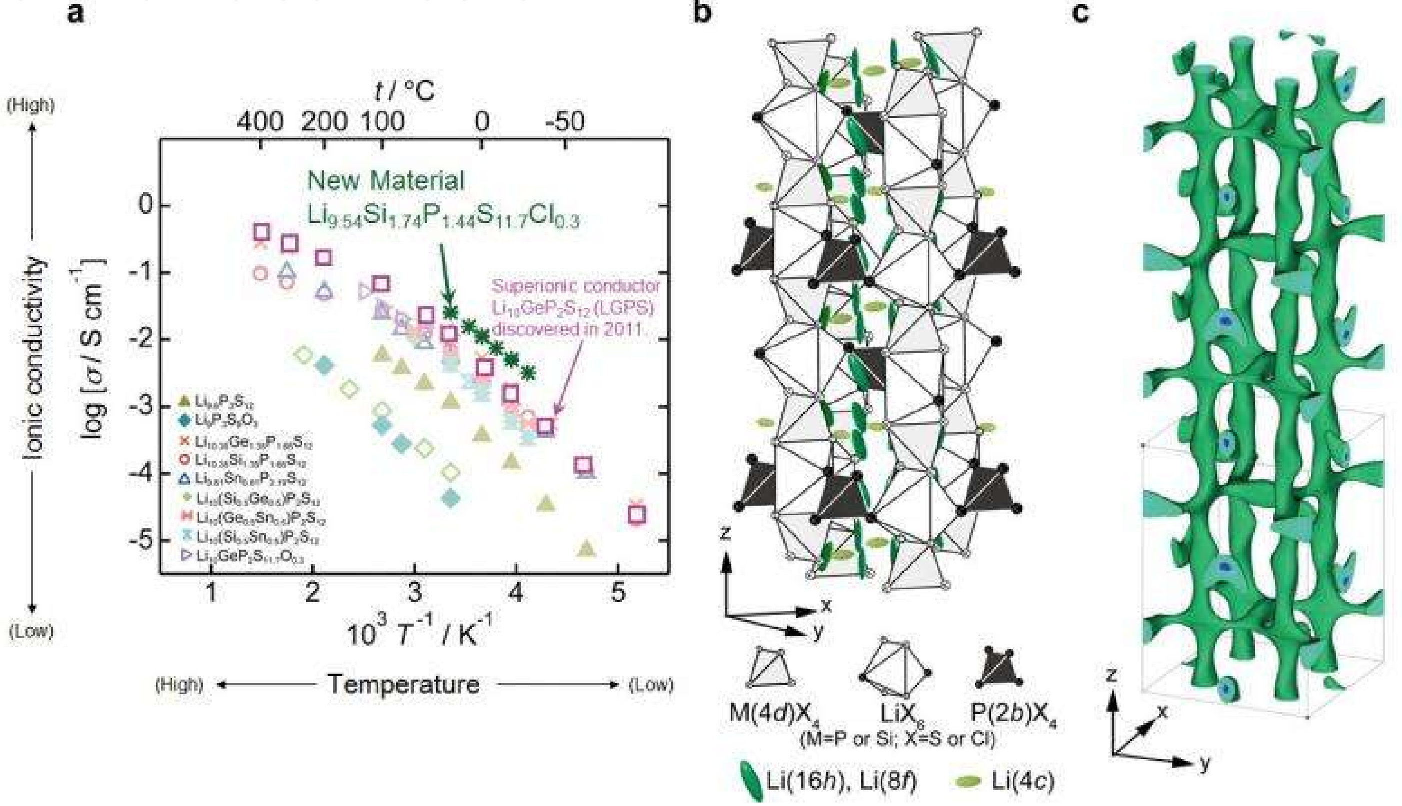


Li-SULFIDE TYPE CRYSTALLINE MATERIAL (THIO-LISICON)

LATEST CLASS OF SUPERIONIC CONDUCTOR

World record of 25 mS/cm at room temperature has been achieved by Japanese groups by substitution and doping of the superionic conductor $Li_{10}GeP_2S_{12}$ *(LGPS) resulting in a crystal structure with widely accessible channels for Li-ion transport*

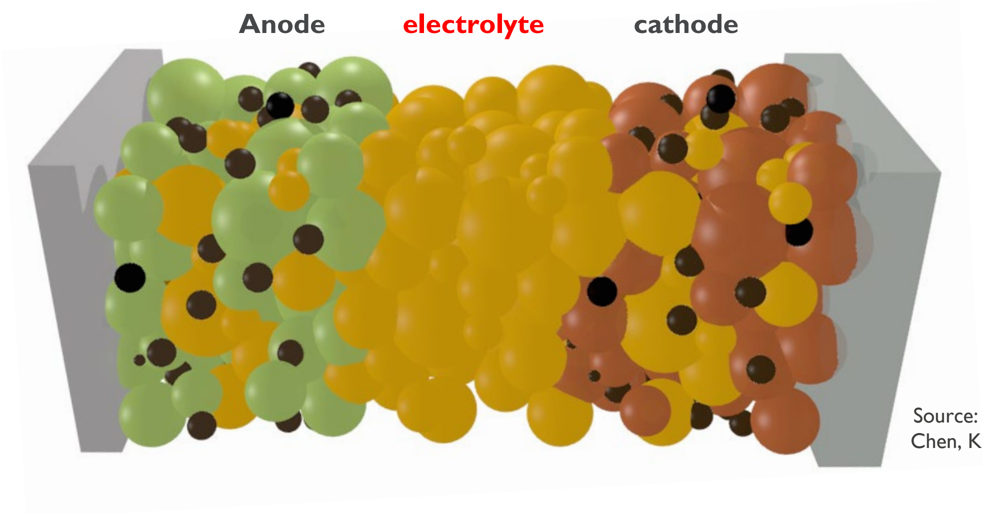


Yuki Kato et al. High-power all-solid-state batteries using sulfide superionic conductors, Nature Energy (2016). DOI: 10.1038/nenergy.2016.30

RESTRICTED USE

SOLID ELECTROLYTE AS “POWDER” LIMITS PERFORMANCE

LOWER CATHODE DENSITY AND “POINT” CONTACTS



Source: PhD thesis of X. Chen, KU-Leuven (2018)

- *Solid electrolyte powder has to be mixed with electrode powder*
  - *Typically as pressed pellet even though also wet coated is possible*
  - *Porosity in the powder pellets/coatings is “lost space”*
  - *Particle size of the electrolyte powder limits the density of the active electrodes*
  - *Ionic interaction only at direct “particle-to-particle” contacts*

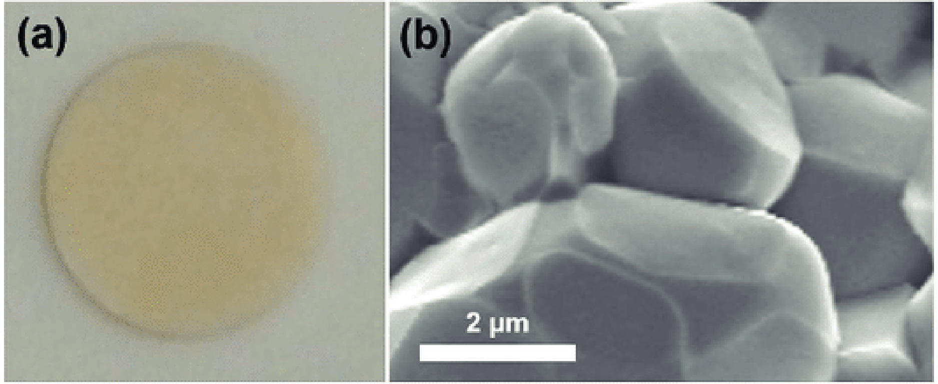
ALSO FOR INORGANIC/CERAMIC SOLID ELECTROLYTES

INTERFACE ENGINEERING FOR “TRANSPARENT” INTERFACES

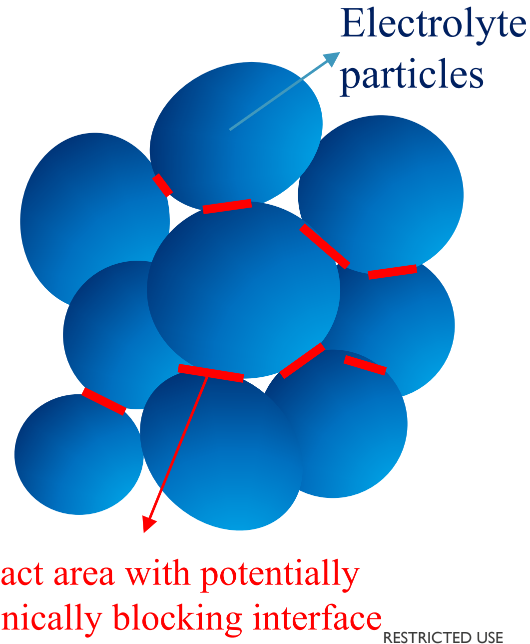
- Pressing and sintering connects the individual particles at certain “contact points” only and thermal (spark) process may create in-diffusion and blocking interfaces

LLZO pellet
(Advanced Materials 29(22):1606042 (2017))

(b)

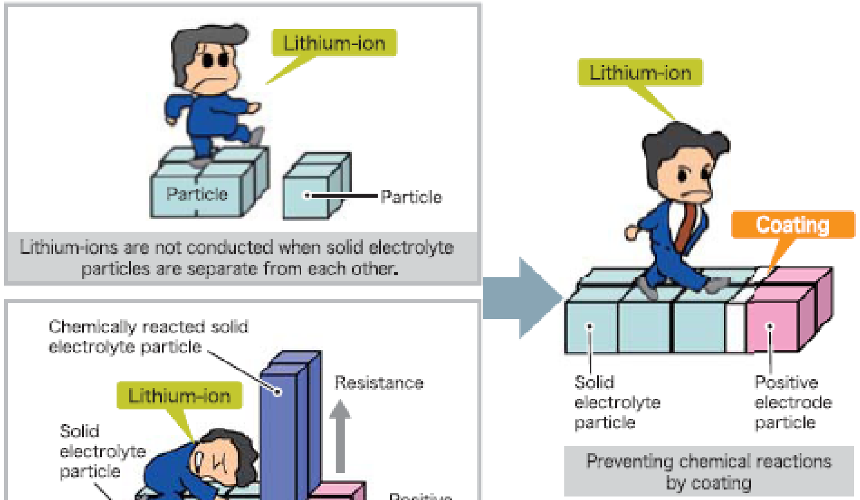


Interface



LIMITED CONTACT AREA AND BLOCKING INTERFACES

ALSO FOR CERAMIC SOLID-STATE COMPOSITE ELECTRODES

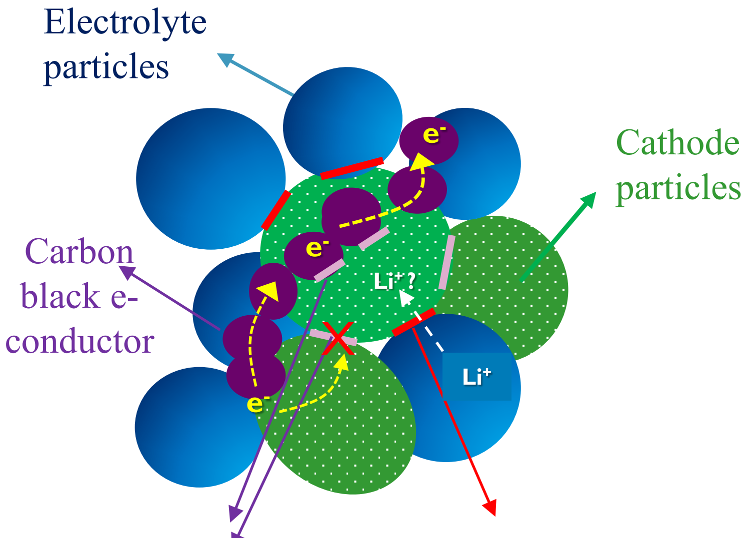


Lithium-ions are not conducted when solid electrolyte particles are separate from each other.

Interface resistance increased by the chemical reaction of solid electrolyte and positive electrode particles

Preventing chemical reactions by coating

(source: Toyota R&D announcement)



Electrolyte particles

Cathode particles

Carbon black e-conductor

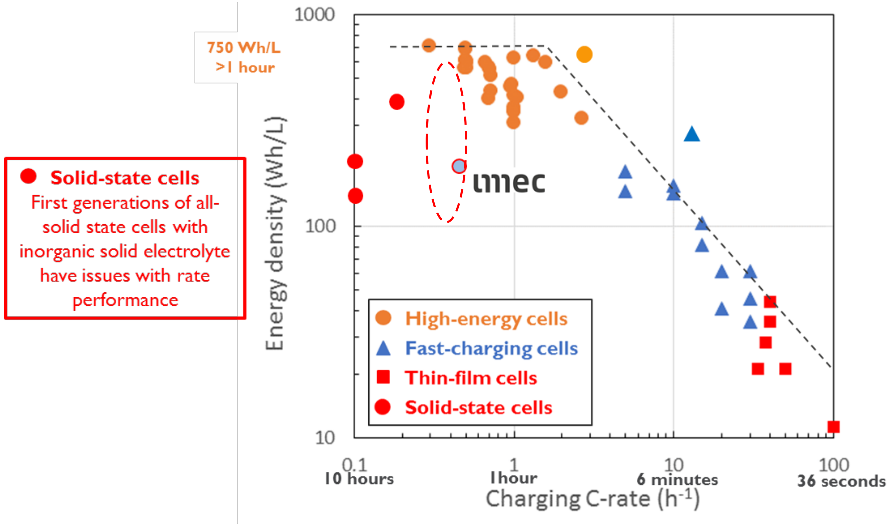
Electronic contact with carbon can be also compromised by interface layers due to sintering process e.g. Similar story for cathode/cathode interface,

Limited contact area for ion access with potentially blocking interface

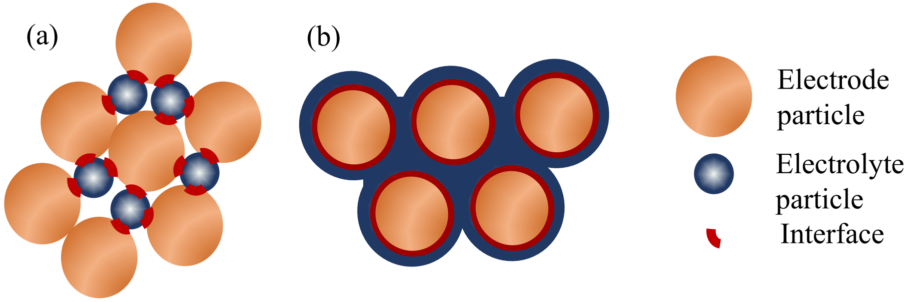
POOR RATE PERFORMANCE

PARTICLE-TO-PARTICLE CONTACT

- In liquids, the active material particles are have maximum contact with electrolyte which is “all around”
- In case of a solid powder electrolyte, the active electrode particles have limited contact points (sintering step to increase the density and contact area)



● Solid-state cells
First generations of all-solid state cells with inorganic solid electrolyte have issues with rate performance



Solid/Solid
point contacts

Solid/Liquid
All-around contact

"Solid and Solid-Like Composite Electrolytes for Lithium Ion Batteries: Engineering the ion conductivity at interfaces", Xubin Chen and Philippe M. Vereecken, Advanced Materials Interfaces, 2018; doi: 10.1002/admi.201800899

HIGH Li-ION CONDUCTIVITY SOLID ELECTROLYTES

- Organic electrolytes (liquid)
  - *Li-salt in carbonate solvent*
  - *Li-salt in Ionic Liquid (ILE)*
- Polymer electrolyte (solid)
  - *Li-salt in PEO*
- *Polymer composite electrolyte*
  - *e.g. TiO_2 NP in PEO*
- Polymer-Gel electrolyte
  - *Polymer with added solvent*
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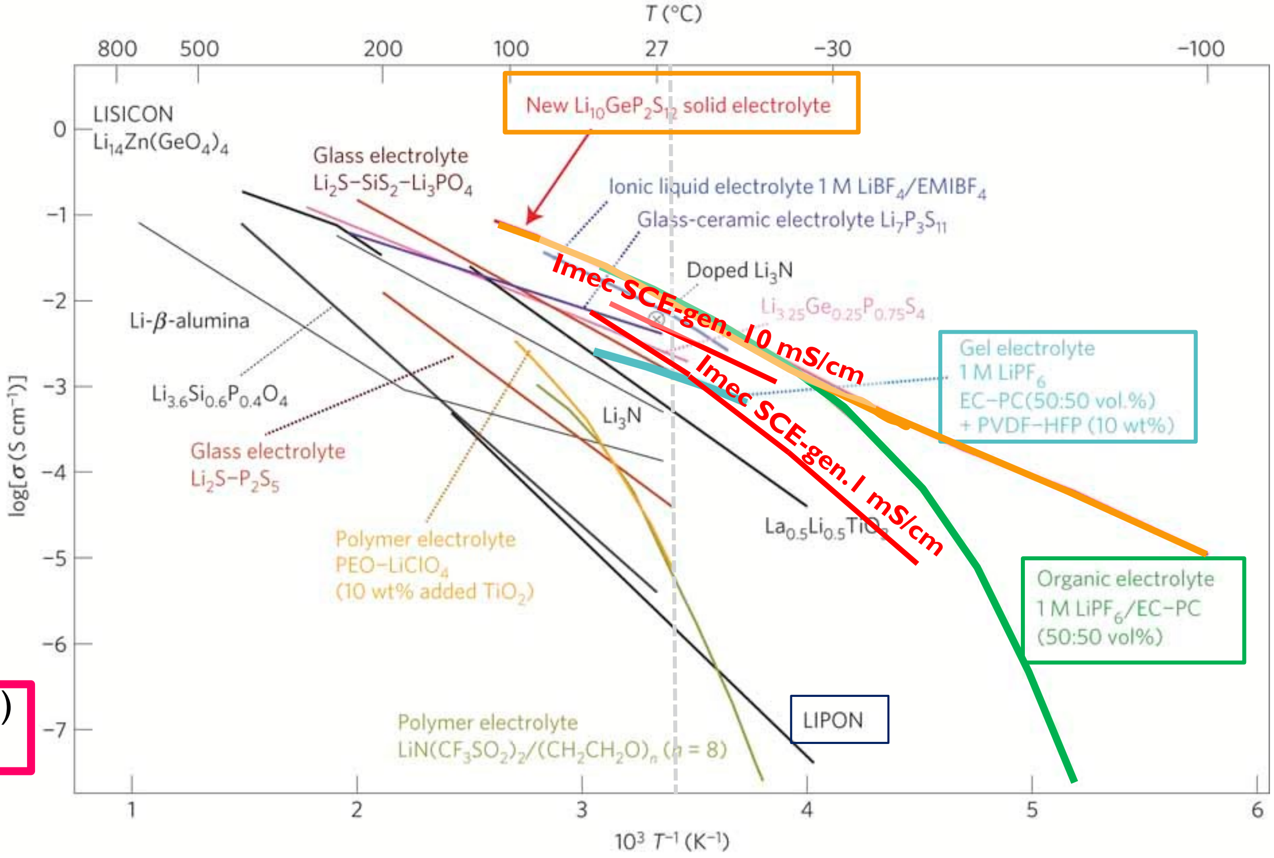


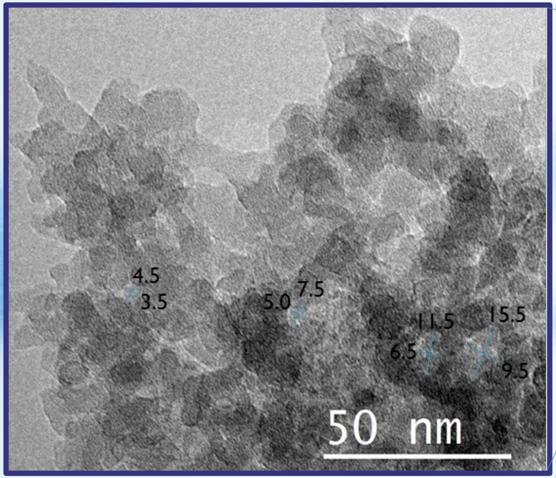
Nature Materials, DOI. 10.1038/NATMAT3066

SOLID NANO-COMPOSITE ELECTROLYTE (NANO-SCE)

ENHANCED ION TRANSPORT AT THE LARGE INTERNAL SURFACE

SCE = *Ionic liquid electrolyte* confined in *mesoporous silica*

SCE monolith pellets



TEM of nanoporous oxide matrix after removal of the electrolyte

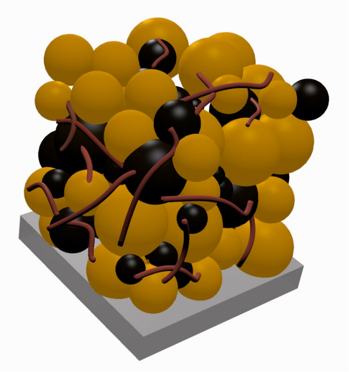
What's unique? The Li-ion conductivity in the composite is enhanced beyond the ion conductivity of the individual Li-ion electrolyte confined in the pores of the porous oxide nanocomposite due to formation of surface adsorbed layer or "mesophase" layer

LIQUID PRECURSOR FOR SOLID ELECTROLYTE

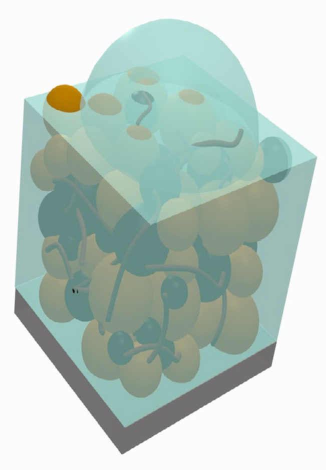
SIMILAR CELL ARCHITECTURES AND SIMILAR MANUFACTURING METHODS

- *Can be manufactured on similar manufacturing tool set as for wet batteries*
- *Similar cell architectures and thus performance*

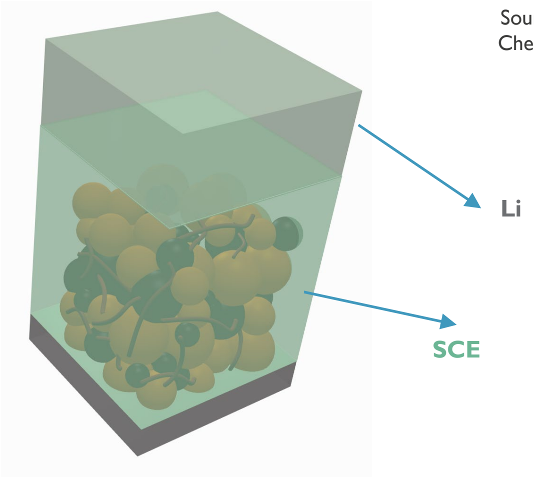
Source: PhD thesis of X. Chen, KU-Leuven (2018)



powder electrode



Impregnated with liquid precursor



After solidification and lamination with anode

IMEC PROCESS FOR NEXT GENERATION BATTERIES

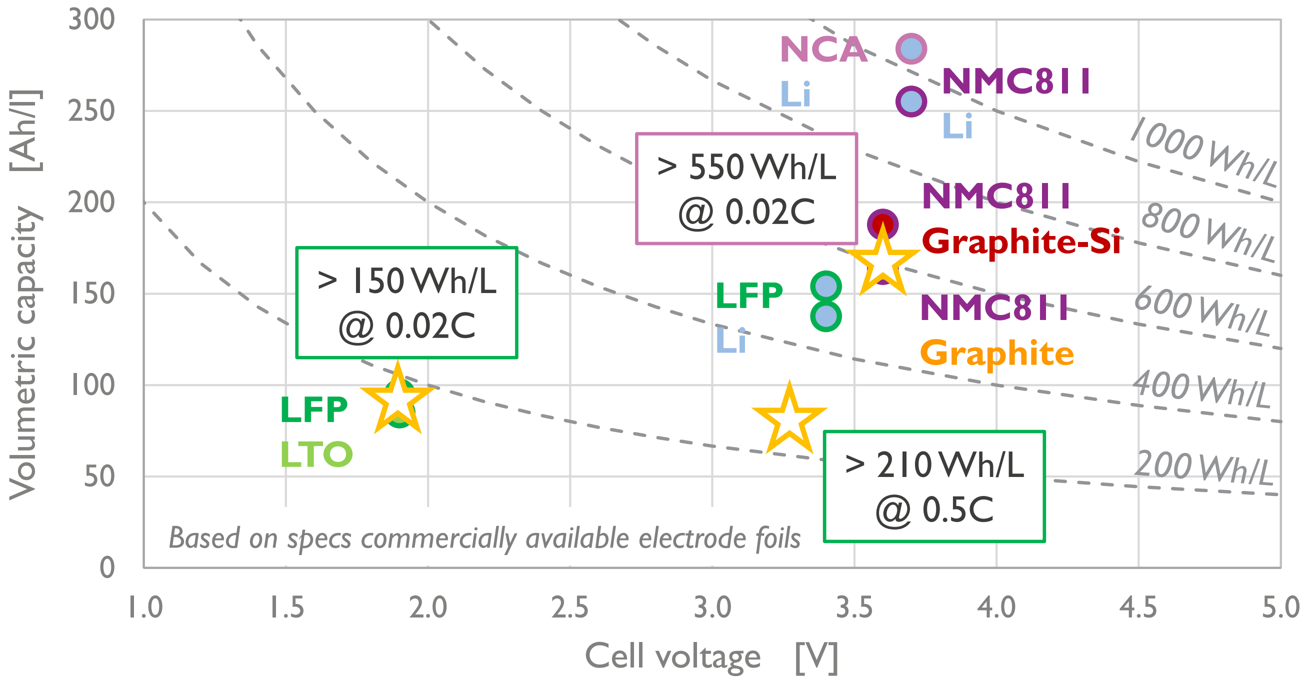
MADE POSSIBLE BY HIGH CONDUCTIVITY NANOCOMPOSITE SOLID ELECTROLYTE

Click on link
For 2min movie

https://www.imec-int.com/en/articles/imec-reaches-milestone-for-next-gen-solid-state-batteries-to-power-future-long-range-electrical-vehicles

STATUS SOLID-STATE LI CELLS

AND CATHODE AND ANODE COMBINATIONS UNDER DEVELOPMENT



> 550 Wh/L
@ 0.02C

> 150 Wh/L
@ 0.02C

> 210 Wh/L
@ 0.5C

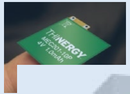
Based on specs commercially available electrode foils

IT’S (OVER)TIME FOR CONCLUSIONS

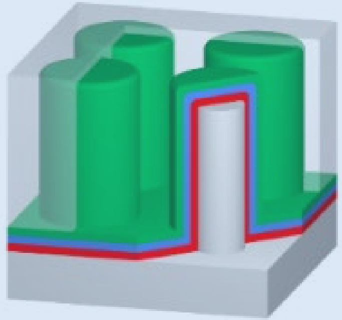
IMEC WORKS ON TWO SOLID-STATE ARCHITECTURES

Rechargeable Li-ion batteries

Power on board



Back-



distri

icators…

Flexible

(2) Solid-state 3D micro battery

with thin-film materials

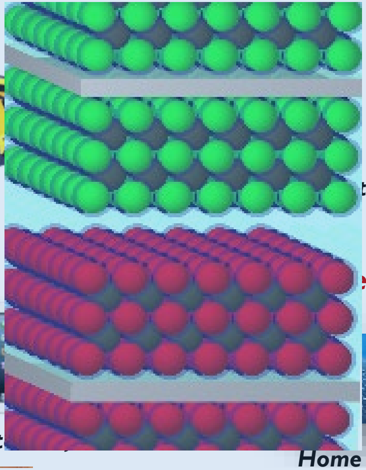
Smart carts, patches, wearables and flexible electronics…

Portable electronics

Hobby and power tools

Mobile-IT

Smart watch, phones, t



tion, rail,…

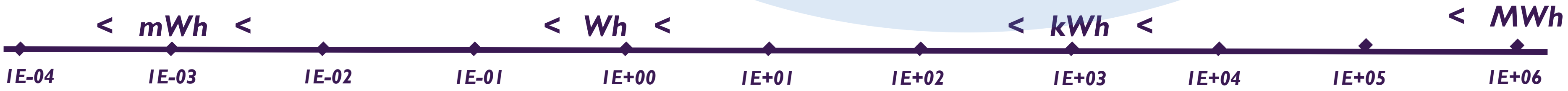
ewable Energy

Home storage, micro-grid storage, grid storage

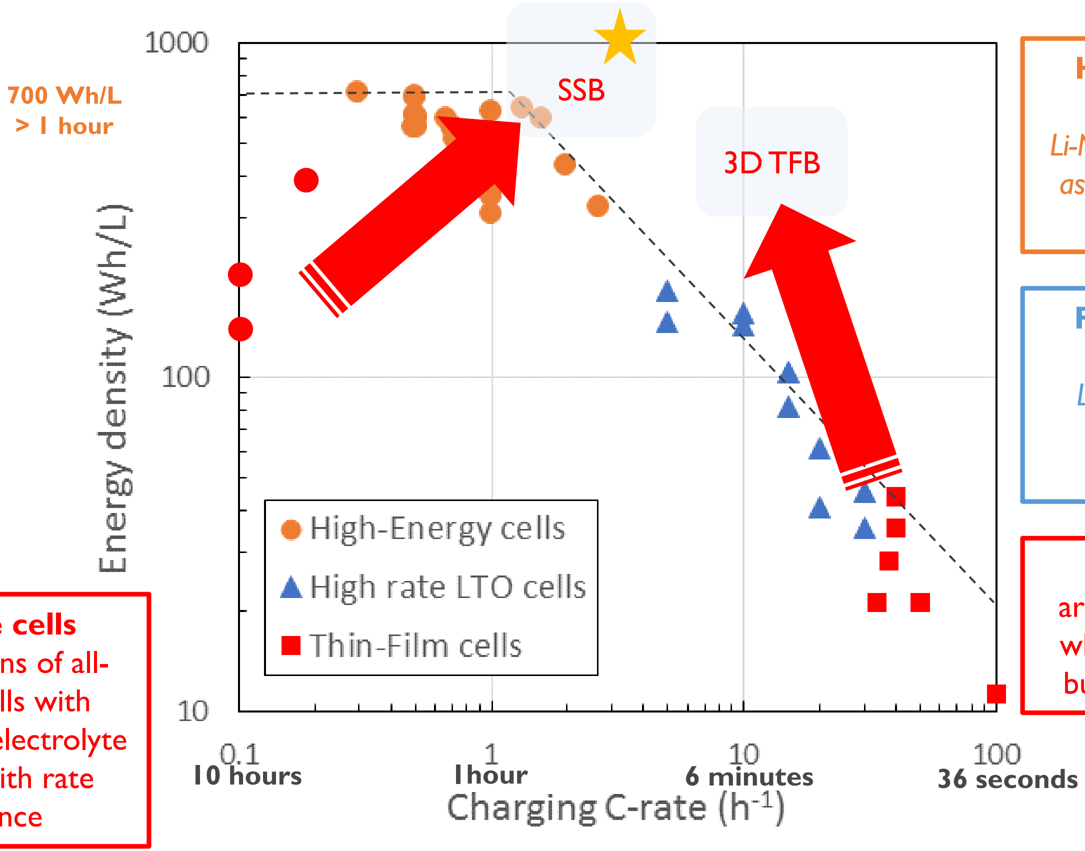
(1) Powder-based Large Energy cells

with imec's wet-casted

Solid nanoComposite Electrolyte (SCE)



CURRENTLY: HIGH ENERGY DENSITY OR FAST CHARGING



High-energy NMC cells (3.6V):
Li-NiMnCo-oxide chemistry as cathode C/Si as anode and liquid electrolyte

Fast-charging LTO cells (2.4V):
LiMn-oxide as cathode LiTi-oxide as anode and liquid electrolyte

Thin-film cells:
are solid-state batteries which give fast charging but low energy density

Solid-state cells
First generations of all-solid state cells with inorganic solid electrolyte have issues with rate performance

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