SOLID STATE BATTERIES:
A STORY ABOUT INTERFACES

PROF. PHILIPPE M. VEREECKEN

Distinguished Member of Technical Staff at imec
Part-time professor at KU-Leuven
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

![Lithium-battery market outlook](source: International Information Technology)

**Steep growth in use of electric cars**

![Electric vehicles and mobile growth](source: De Tijd)

**New technologies coming**

Source: De Tijd
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...

- Portable electronics
- Automotive
- Storage
- IoT
- Wearables
- Health
- Flexible electronics

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

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

And will continue to do so for future electronics.
APPLICATION SPECTRUM OF Li-ION BATTERIES

Rechargeable Li-ion 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

---

Rechargeable Li-ion batteries are used in various applications including:

- **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

The spectrum of applications ranges from micro-level energy (in mWh) to macro-level energy (in MWh).
• 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

- negative electrode (anode)
- positive electrode (cathode)
- separator
LITHIUM ION CELL WITH LIQUID ELECTROLYTE

THE CELL IS LITERALLY SOAKED WITH LIQUID ELECTROLYTE SOLUTION

- Copper foil
- Graphite/Si composite anode
- Separator + liquid electrolyte
- Particle composite Cathode impregnated with liquid electrolyte
- Aluminum foil
- State-of-the art liquid cell
- Liquid electrolyte fills the porous electrode
- Binder
- Carbon black conductive agent
- Active micro-powder
### Cathode Material vs. Li⁺/Li

<table>
<thead>
<tr>
<th>Material</th>
<th>V vs. Li⁺/Li</th>
<th>Gravimetric Capacity</th>
<th>Volumetric Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNi₀.₈Co₀.₁₅Al₀.₀₅O₂ (NCA)</td>
<td>3.8 V</td>
<td>180-200 Ah/kg</td>
<td>800-890 Ah/L</td>
</tr>
<tr>
<td>LiCo₁/₃Ni₁/₃Mn₁/₃O₂ (NMC)</td>
<td>3.9 V</td>
<td>160-170 Ah/kg</td>
<td>760-810 Ah/L</td>
</tr>
<tr>
<td>LiCoO₂ (LCO)</td>
<td>3.9 V</td>
<td>140 Ah/kg</td>
<td>710 Ah/L</td>
</tr>
<tr>
<td>LiFePO₄ (LFP)</td>
<td>3.4 V</td>
<td>170 Ah/kg</td>
<td>610 Ah/L</td>
</tr>
<tr>
<td>LiMn₂O₄ (LMO)</td>
<td>4.1 V</td>
<td>148 Ah/kg</td>
<td>650 Ah/L</td>
</tr>
</tbody>
</table>

### Anode Material vs. Li⁺/Li

<table>
<thead>
<tr>
<th>Material</th>
<th>V vs. Li⁺/Li</th>
<th>Gravimetric Capacity</th>
<th>Volumetric Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₄Ti₅O₁₂ (LTO)</td>
<td>1.55V</td>
<td>160 Ah/kg</td>
<td>650 Ah/L</td>
</tr>
<tr>
<td>Li₄Si (silicon)*</td>
<td>0.27 V</td>
<td>3580 Ah/kg</td>
<td>2190 Ah/L</td>
</tr>
<tr>
<td>LiC₆ (graphite)</td>
<td>0.15 V</td>
<td>370 Ah/kg</td>
<td>840 Ah/L</td>
</tr>
</tbody>
</table>

**Liquid Electrolytes**

- lithium salts, such as LiPF₆, LiBF₄ or LiClO₄ 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).

* Currently, only composites of Si(<10%) with graphitic carbon are commercially available.
Li-ION CELL WORKS BY “ION INTERCALATION”
SOLID-STATE ELECTROCHEMISTRY AT WORK

Graphite
Negative Electrode
(0.15V)

Electrolyte

LiCoO₂
Positive Electrode
(3.9V)

Solid-state diffusion

Diffusion though liquid or solid electrolyte

Solid-state diffusion

Ion transfer at electrode/electrolyte interface

Ion transfer at Electrolyte/electrode interface

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)

\[
Li_{1-x}CoO_2 + xLi^+ + xe^- \rightleftharpoons LiCoO_2
\]

Reduced state with valence of Cobalt (+III)

\[
-(C_6 + xLi^+ + xe^- \rightleftharpoons Li_xC_6)
\]

Cell reaction: \( Li_{1-x}CoO_2 + Li_xC_6 \rightleftharpoons LiCoO_2 + C_6 \)

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 LiCoO₂ crystal to compensate the gain in positive charge upon oxidation of Co(III) to Co(IV)

Li⁺ ions are inserted into the layered LiCoO₂ crystal to compensate the loss in positive charge upon reduction of Co(IV) to Co(III)

Oxidized state with valence of Cobalt (+IV)

\[ Li_{1-x}CoO_2 + xLi^+ + xe^- \rightleftharpoons LiCoO_2 \]

Reduced state with valence of Cobalt (+III)

\[ -(C_6 + xLi^+ + xe^- \rightleftharpoons Li_xC_6) \]

Cell reaction:

\[ Li_{1-x}CoO_2 + Li_xC_6 \rightleftharpoons LiCoO_2 + C_6 \]

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) $\leftrightarrow$ 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 $\sim 45$ A-h/kg

Voltage $\sim 3.7$ Volts

Energy density $\sim 165$ W-h/kg

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

*Anisotropic lithiation kinetics (depends on crystal orientation)!*
The spinel structure of \( \text{Li}_{1-x}\text{Mn}_2\text{O}_4 \) is characterized by Mn ions occupying the octahedral sites, while Li\(^+\) resides on the tetrahedral sites. This structure is rather poor in electrical conductivity.

Lithium de-intercalation varies from \( 0 \geq x \geq 1 \), comparable to \( \text{Li}_{1-x}\text{CoO}_2 \). Presence of Mn\(^{3+}\) gives a Jahn-Teller distortion that limits cycling. High Li content stabilizes a layer-like structure.

- **Capacity**: \(~ 36 \text{ A-h/kg}~\)
- **Voltage**: \(~ 3.8 \text{ Volts}~\)
- **Energy density**: \(~ 137 \text{ W-h/kg}~\)

Mn is cheap and non-toxic. Lithiation kinetics are independent of crystal orientation.
Energy density increasing strategies

- 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

NMC = LiNi$_x$Mn$_y$Co$_z$O$_2$

Source: Kurt Vandeputte (Umicore), ITF presentation, 23-24 May 2018, Antwerp, Belgium
“5V” cathode materials

For increased energy

Issues with electrolyte stability

Li-rich cathode materials

For increased capacity

Issues with electrode 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
\( \text{Al}_2\text{O}_3 \) IS THE MOST COMMONLY APPLIED PROTECTIVE COATING

(FIRST) \( \text{Al}_2\text{O}_3 \) COATING OF LiCoO\(_2\)

- \( \text{Al}_2\text{O}_3 \) coating on the full electrode greatly improves cyclability → attributed to the formation of an artificial CEI
- \( \text{Al}_2\text{O}_3 \) coating directly on particles blocks electronic access
- Coating cannot be made too thick as \( \text{Al}_2\text{O}_3 \) is an ionic insulator
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
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
PROTECTIVE COATINGS HELP AGAINST INTERFACE DEGRADATION
ALD/MLD FOR COATING INSIDE THE POROUS ELECTRODES

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$_2$O$_3$ does

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

(source: Toyota R&D announcement)
SOLID STATE BATTERIES STILL REQUIRE PROTECTIVE COATINGS
EXAMPLE TOYOTA 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)

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$_2$O$_4$ cathode improves cyclability by preventing Mn$^{3+}$ dissolution
  - Thin-film am-TiO$_2$ coating on LMO enhances the rate performance

---


SOLID-STATE AND LITHIUM METAL FOR NEXT GENERATION BATTERIES
• 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

- 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
- 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

- 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
- Currently leveling off towards practical ceiling of 800Wh/L by 2025
- Switch to solid-state needed to surpass the 800Wh/L ceiling and reach the goal of 1000Wh/L in 2030
• 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
• Currently leveling off towards practical ceiling of 800Wh/L by 2025
• Switch to solid-state needed to surpass the 800Wh/L ceiling and reach the goal of 1000Wh/L in 2030
SOLID ELECTROLYTE ENABLES METALLIC LITHIUM
THE PRINCIPLE IS SIMPLE – CREATE MORE SPACE IN THE CELL ARCHITECTURE

650 Wh/L

Solid electrolyte

1000 Wh/L

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

NMC cathode
Graphite anode

NMC cathode
Lithium anode
ELECTRODE MATERIAL SET PRACTICAL UPPER LIMIT
SOLID STATE EXTENDS THE PRACTICAL LIMIT FOR Li-ION CELLS

More cathode material can be stacked in the same volume through changes of cell architecture:
- Thinner (Li) anode
- Thinner separator
- Denser cathode?
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 50\(\Omega \cdot \text{cm}^2\)


define li-ion conductivity (S/cm)
define thickness (\(\mu\text{m}\))

- 100% Electrolyte
- 50% Porosity
- 20% Porosity
- 10% Porosity

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

Thin-Film battery \(\sigma > 10^{-7} \text{ S/cm}\)

Powder battery \(\sigma > 10^{-3} \text{ S/cm}\)
**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. TiO₂ 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 1 and 10 mS/cm is needed to match current liquid cell technology.
TOP-10 REQUIREMENTS FOR SOLID ELECTROLYTE COMPONENT
DIFFERENT SOLID-STATE ELECTROLYTES GIVE DIFFERENT PROPERTIES

1. High ionic conductivity ($\sigma_1 > 10^{-3}$ S/cm for large capacity batteries)
2. Wide electrochemical window ($0 < V$ vs. Li$^+/\text{Li} < 5.5$)
3. Chemical stability (temperature, against electrodes and metallic Li)
4. Wide temperature range (-40C $\leftrightarrow$ 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)
The battery stack consists of a LiMn$_2$O$_4$ 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 $\sigma_{Li}$

- Organic electrolytes (liquid)
  - Li-salt in carbonate solvent
  - Li-salt in Ionic Liquid (ILE)
- Polymer electrolyte (solid)
  - Li-salt in PEO
- Polymer composite electrolyte
  - 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
NITROGEN-DOPED LITHIUM PHOSPHATE GLASS (LiPON)

PE-ALD LiPON films

- Doping of amorphous Li$_3$PO$_4$ 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
“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

- 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 5μm thickness)

Higher capacity
Slower charging

Lower capacity
Faster 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”
Capacity vs. Film thickness

“Aspect-ratio scaling”
Capacity vs. Pillar height
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/cm³
- **Fast charging:** 80% max. capacity in 3 min charging (20C)
- **Safety & Stability**

**Our solution:**

3D Solid-State Thin-Film Batteries
FOOTPRINT CAPACITY > 2mAh/cm²
CAPACITY DENSITY > 100mAh/cm³

- 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)

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: 50-60 µm

Area enhancement of 20-25x
OUR 3D THIN-FILM STACK

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

PERFORMANCE OF OUR 3D Cl-doped TiO₂ THIN-FILM ELECTRODE

Same rate performance for 3D and planar electrodes but with 24 times higher capacity for the 3D TiO₂ electrode

PRINCIPLE WORKS

PERFORMANCE OF OUR 3D LiMn$_2$O$_4$ THIN-FILM ELECTRODE

- First demonstration of a 3D LMO electrode

Same rate performance for 3D and planar electrodes but with 21 times higher capacity for the 3D LMO electrode.
3D THIN-FILM ELECTRODE STATUS
LMO AND DOPED TITANIA HALF CELLS PLOTTED TOGETHER

- 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

Double the capacity of best planar thin-film battery and with ~60mA/cm³ already better than coin cells
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
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 $5 \times 10^{-7} \text{ S/cm}$ at 300K
First to demonstrate a planar thin-film battery with ALD LiPON
Next, a full 3D cell will be built

PLANAR THIN-FILM BATTERY WITH ALD LiPON

- First battery employing ultra thin ALD LiPON
- $R = 15 \, \Omega \cdot \text{cm}^2$
- Reaches 87 mAh/g
- Li metal in contact with 70 nm LiPON is stable

Two-step deposition for SCE

- Deposit porous silica film
- Fill pores with polymer electrolyte by spin coating


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.
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

- 100% Electrolyte
- 50% Porosity
- 20% Porosity
- 10% Porosity

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

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

Li-ion conductivity (S/cm)

thickness (μm)

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 – \( \text{Li}_{0.5}\text{La}_{0.5}\text{TiO}_3 \) OR LLTO

RECORDHOLDER FOR MANY YEARS WITH RT ION CONDUCTIVITY \( \sim 1 \text{mS/cm} \)

- 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
GARNET – Li$_7$La$_3$Zr$_4$O$_{12}$ OR LLZO

RT ION CONDUCTIVITY BETWEEN 0.1-1 mS/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

**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

$\text{Li}_{10}\text{GeP}_{2}\text{S}_{12}$ WITH RT ION CONDUCTIVITY OF $\sim 10 \text{ mS/cm}$

- 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
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 \( \text{Li}_{10}\text{GeP}_2\text{S}_{12} \) (LGPS) resulting in a crystal structure with widely accessible channels for Li-ion transport.
SOLID ELECTROLYTE AS “POWDER” LIMITS PERFORMANCE
LOWER CATHODE DENSITY AND “POINT” CONTACTS

- **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

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

(Advanced Materials 29(22):1606042 (2017))
Limited contact area and blocking interfaces also for ceramic solid-state composite electrodes.

Electronic contact with carbon can be also compromised by interface layers due to sintering process e.g. Similar story for cathode/cathode 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 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
- **Inorganic crystalline SE**
  - LiSICON, LLTO, Garnet
- **Inorganic glass SE**
  - LiPON
- **Solid Composite Electrolyte (SCE)**
  - Silica and alumina with Li-salt
  - MOFs

*Image: Graph showing the conductivity of various electrolytes. The graph includes labels for different electrolyte types and their conductivity values. The graph includes a text box with the title '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

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

IMEC PROCESS FOR NEXT GENERATION BATTERIES
MADE POSSIBLE BY HIGH CONDUCTIVITY NANOCOMPOSITE SOLID ELECTROLYTE

STATUS SOLID-STATE LI CELLS
AND CATHODE AND ANODE COMBINATIONS UNDER DEVELOPMENT

Based on specs commercially available electrode foils

<table>
<thead>
<tr>
<th>Material</th>
<th>Volumetric Capacity [Wh/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>LFP</td>
<td>&gt; 210 @ 0.5C</td>
</tr>
<tr>
<td>LTO</td>
<td></td>
</tr>
<tr>
<td>NMC811 Graphite</td>
<td>&gt; 550 @ 0.02C</td>
</tr>
<tr>
<td>NMC811 Graphite-Si</td>
<td></td>
</tr>
<tr>
<td>NCA Li</td>
<td></td>
</tr>
<tr>
<td>LTO Li</td>
<td></td>
</tr>
<tr>
<td>LFP Li</td>
<td></td>
</tr>
</tbody>
</table>
IT’S (OVER)TIME FOR CONCLUSIONS
IMEC WORKS ON TWO SOLID-STATE ARCHITECTURES

Rechargeable Li-ion batteries

1. **(1) Powder-based Large Energy cells**
   - with imec’s wet-casted Solid nanoComposite Electrolyte (SCE)
   - Smart carts, patches, wearables and flexible electronics...
   - Hobby and power tools
   - Mobile-IT
   - Renewable Energy
   - Home storage, micro-grid storage, grid storage

2. **(2) Solid-state 3D micro battery**
   - with thin-film materials
   - Smart cards, patches, wearables and flexible electronics...
   - Back-up power chip or PCB
   - Portable electronics
   - Power on board
   - Hobby and power tools
   - Mobile-IT
   - 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 |
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

**Energy density (Wh/L)**
- 700 Wh/L > 1 hour

**Charging C-rate (h⁻¹)**
- 0.1 hours to 1 hour
- 10 minutes to 36 seconds

---

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
ACKNOWLEDGEMENTS

- Estore team, imec-Leuven
  - Nathalie Hendrickx
  - Nick Clerckx
  - Dr. Maarten Mees
  - Dr. Brecht Put
  - Dr. Xubin Chen
  - Dr. Maarten Debeucquoy
  - Dr. Knut Gandrud
  - Nouha Labyedh
  - Stanislav Zankowski
  - Simon Hollevoet
  - Louis De Taeye
  - Eva Vandaele
  - Dr. Yongho Kee
  - Andrea Pitillas Martinez
  - Keerthi Reddy
  - Genis Vanheusden
  - Dr. Sergey Remizov
  - Akihiko Sagara

- Bart Onsia, Dr. Geoffrey Pourtois, Prof. Paul Heremans
- Prof. Christophe Detavernier and team, University Ghent
embracing a better life