Experiences of PLD Technology for LIB Separators

PICODEON Oy

Neal White

Outline

Introduction to Picodeon

Ceramic coating rationale

Separator overview

Why PLD for LIB separators

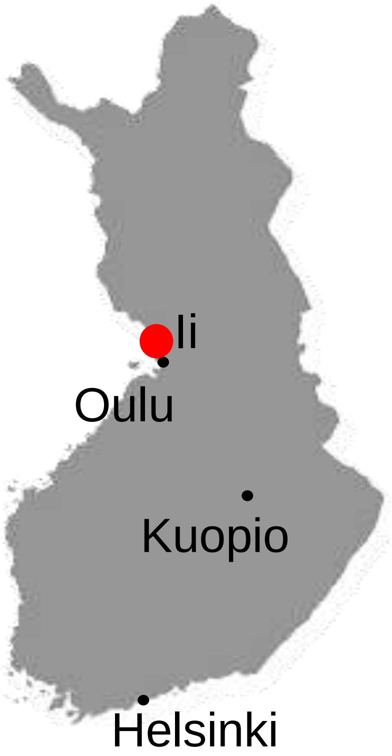
Current status of Picodeon PLD coated LIB separators

Summary

Acknowledgements

Company Background

- Founded 2005
- Technology and customer service centre in Ii Finland with state-of-the-art US PLD facilities
- Strong IPR portfolio containing 19 patent families
- R&D supported by excellent technology and research ecosystem (e.g. universities) in Finland and Oulu region
- Multidisciplinary Ph.D., M.Sc. Technical Team



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PLD Technology and Application Overview

Applications		Technology: Present	Technology: New
Applications	New	**3** **Near Future < 18 mos** Technology: Porous Application: PEM Fuel cells	**4** **Roadmap > 18 mos** Technology: Porous & Dense Application: OLED Metals Tribological
Applications	Present	**1** **Core** Technology: Porous Application: LIB Separator Sensors Customer: Validation in progress	**2** **Enablers** • In-situ process metrology • Engineered targets • R2R coating • In-house metrology • Optics and lasers

Present **New**

Technology

PEM = Polymer Electrolyte Membrane

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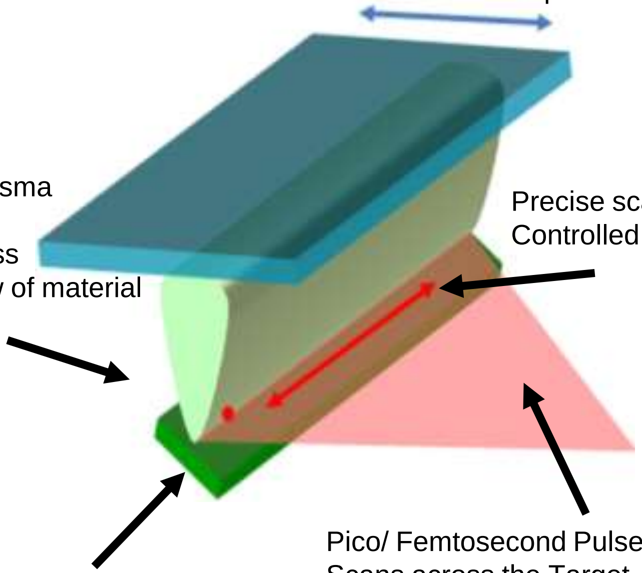
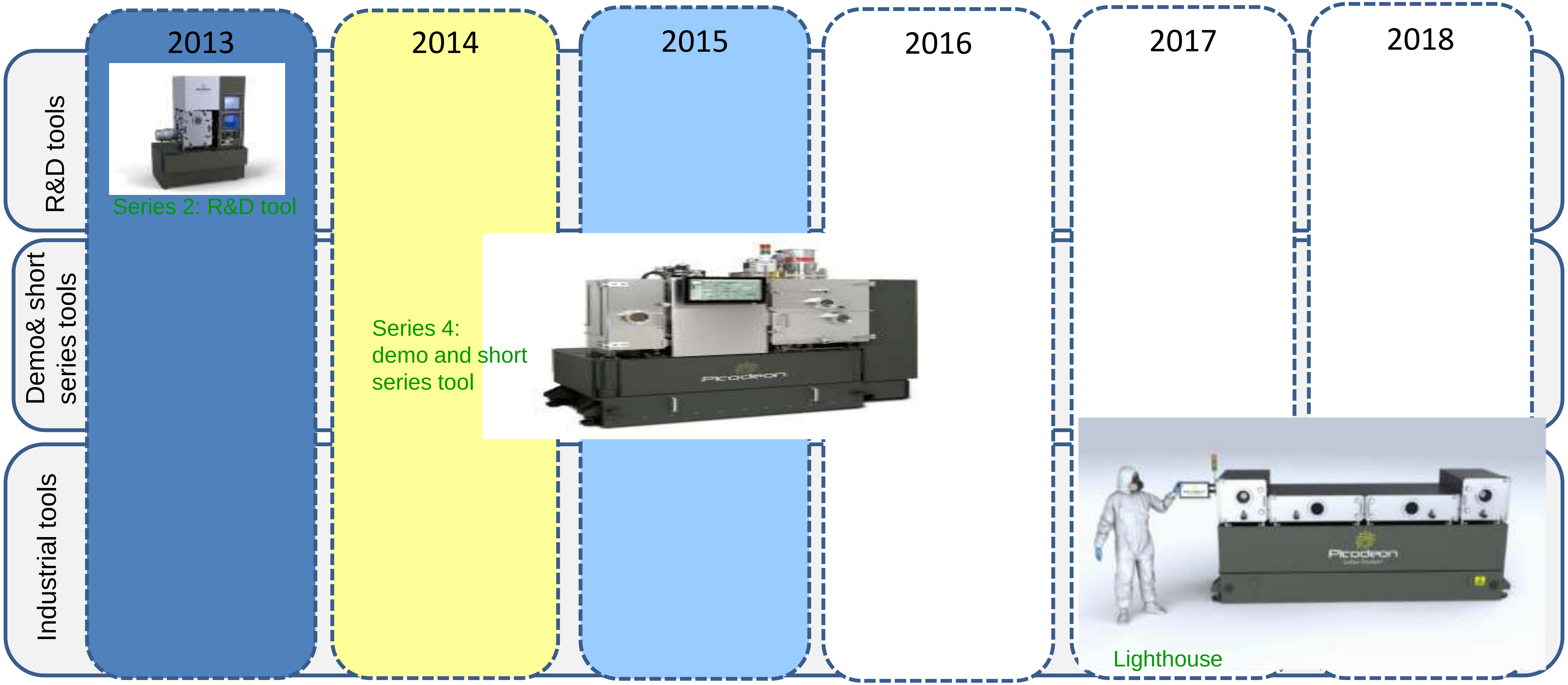
Picodeon Coldab®

Pulsed Laser Deposition (PLD)



Platform Road Map



Why Ceramic Coating?

Better Adhesion

Thermal Runaway

Lower Shrinkage

Safety

Separator Oxidation

Dendrite Growth

Same Material

Stability on the Path to 5V......

No Binder

Lower Ionic Resistivity

Thin Film Capability

Better Thickness Uniformity

Electrolyte Stabilization

Electrode Interface Improvement

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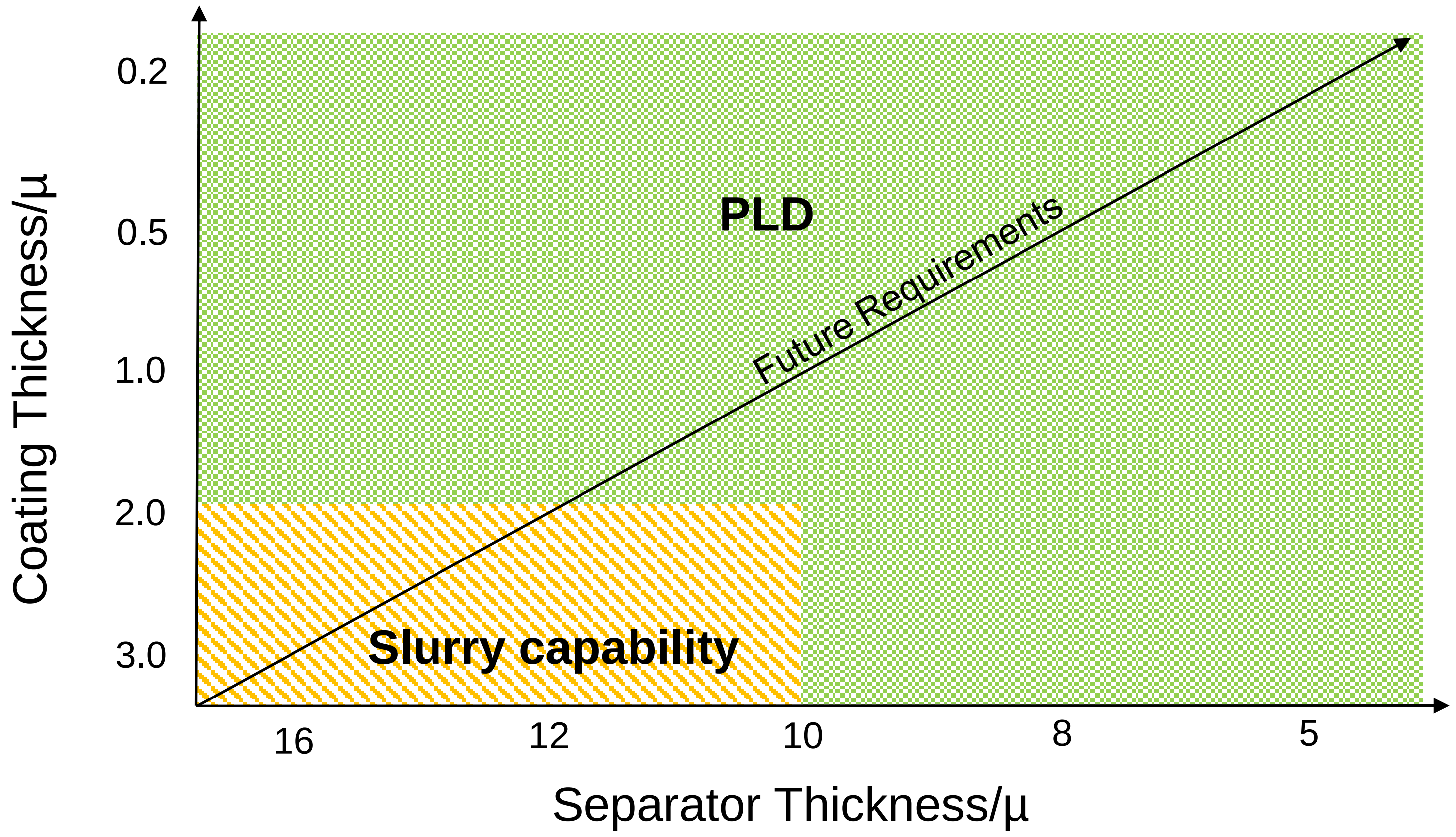
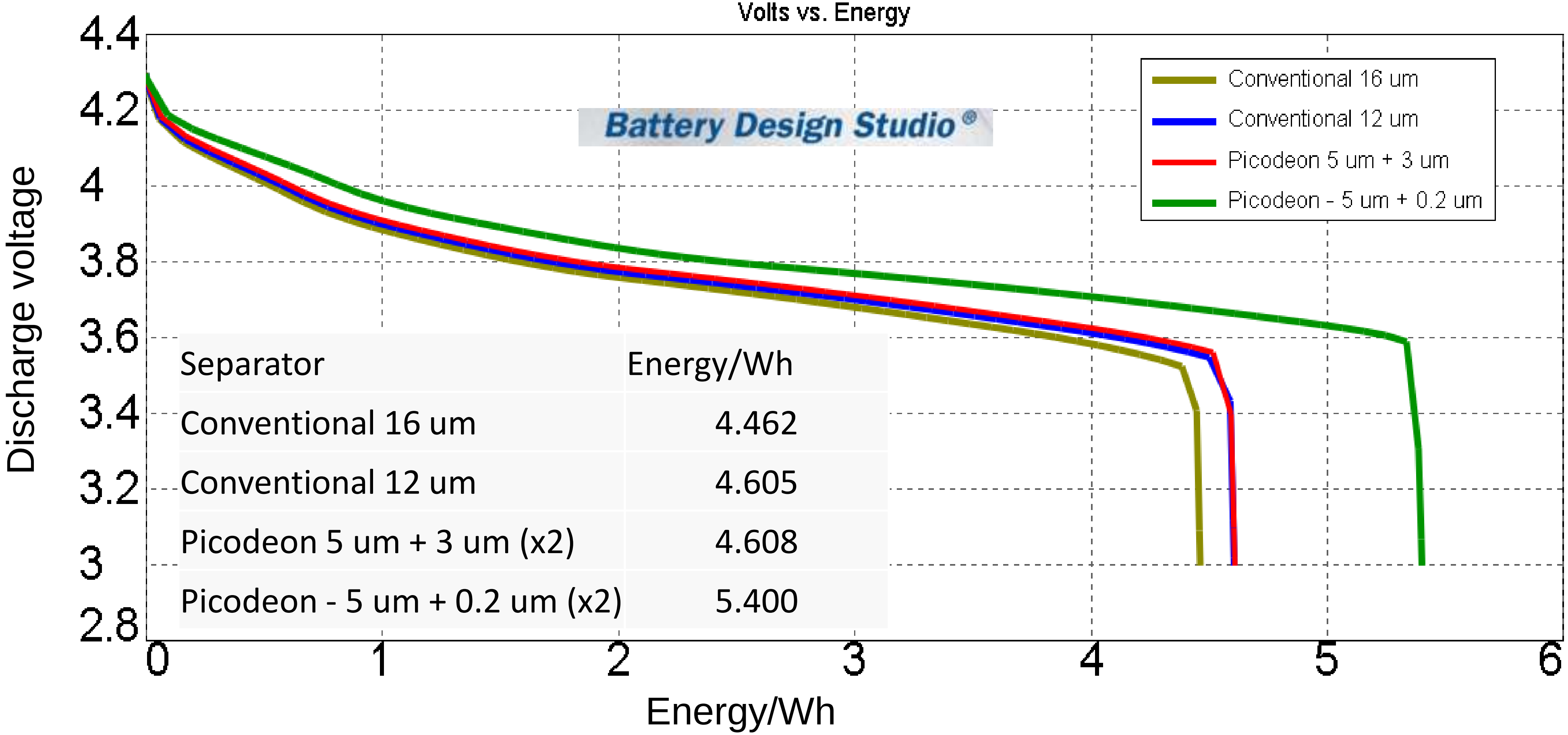
Coating Requirements



Effect of Separator Thickness on Cell Energy

1.5 A Discharge



Separator	Energy/Wh
Conventional 16 um	4.462
Conventional 12 um	4.605
Picodeon 5 um + 3 um (x2)	4.608
Picodeon - 5 um + 0.2 um (x2)	5.400

5.4 micron thick separator enables 20% increase in energy

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Required properties of Separators

Functional Properties

Property	Function
Ionic conductor	To allow solvated lithium transport between anode and cathode
Electronic insulator	To prevent short circuit and leakage current
High Porosity	Low blocking of ionic transport
Small Pore size	Prevent solid particle transport and shorting
Chemical Stability	For long shelf and high cycle life. No reaction with anode, cathode or electrolyte
Puncture strength	To prevent penetration of active material during charge and discharge - dendrites

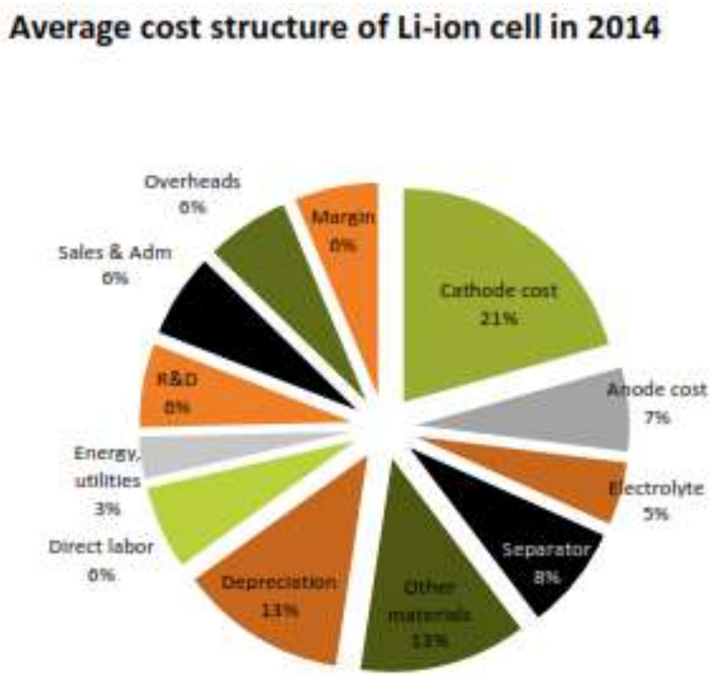
Safety related Properties

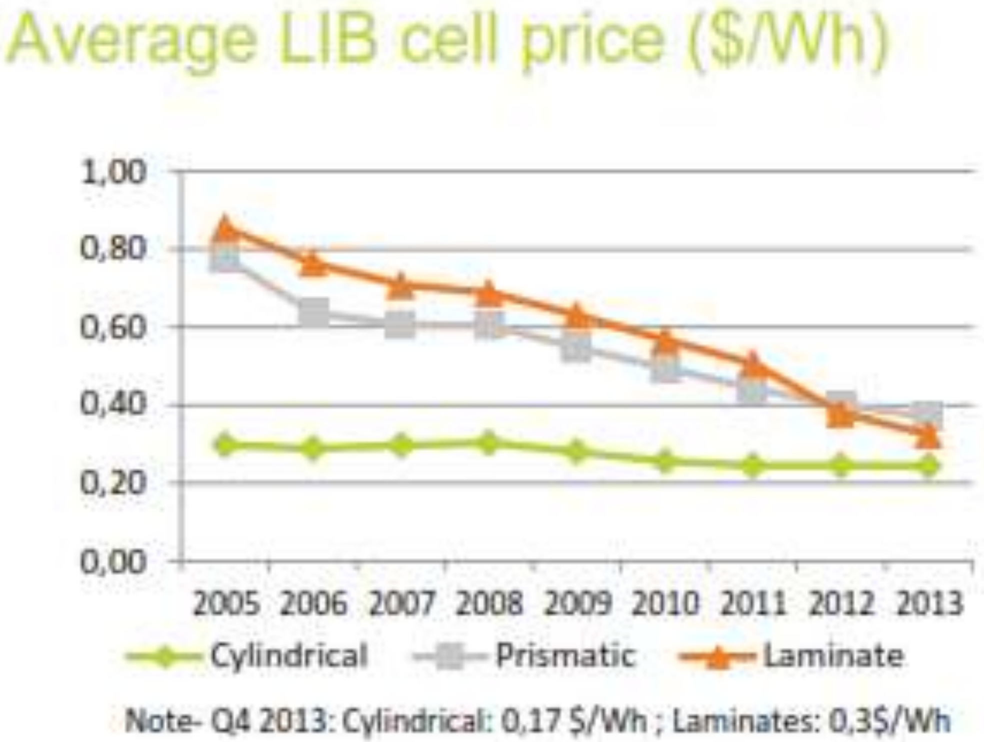
Property	Safety benefit
Low Thermal shrinkage	To prevent anode and cathode coming into contact at elevated temperature
Puncture strength	Prevention of active material penetration and contact
Thermal shutdown	Mitigation of thermal runaway
Uniform permeability	Avoidance of dry areas and charge/discharge hot/cold spots

Performance/Production related properties

Property	Performance/Production benefit
Tensile strength	Enables fast winding
Wettability	For rapid cell filling and electrolyte retention in the active region
Flatness	Essential for efficient winding
Uniform high electrolyte permeability	Even charge/discharge, maximises capacity
Thinness	Increased active material volume – higher capacity
Low cost	Reduced production costs

Cost structure and price decline for LIB





Avicenne 2015

Cost is continually falling – without a disruptive technology LIB are simple commodities, price is determined by market not cost of manufacture

ANL BatPaC Dec 2015 has separator price at $1.2 m^2$

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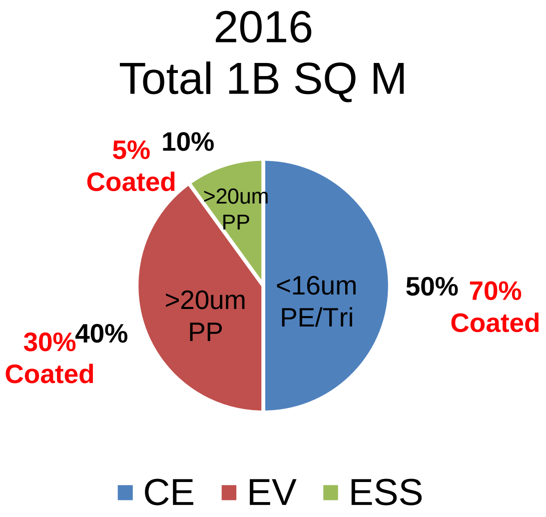
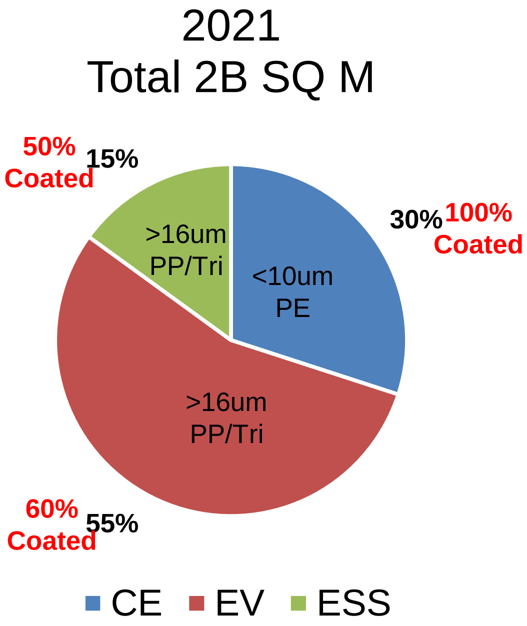
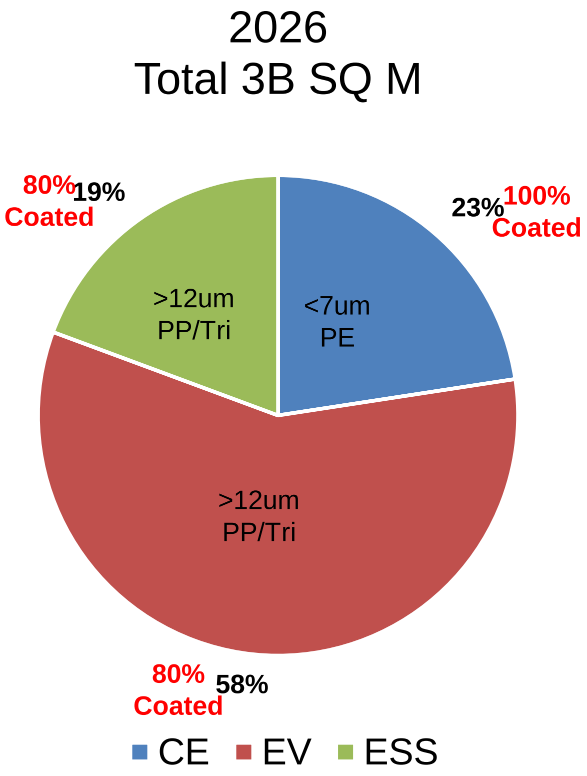
LIB Separator Market







What is PLD and why is it useful for coating LIB separators?

Pulsed **L**aser **D**eposition is a method of removing target material (ablation) in a controlled way at low temperature

Many ceramic materials can be used – Alumina is the most common

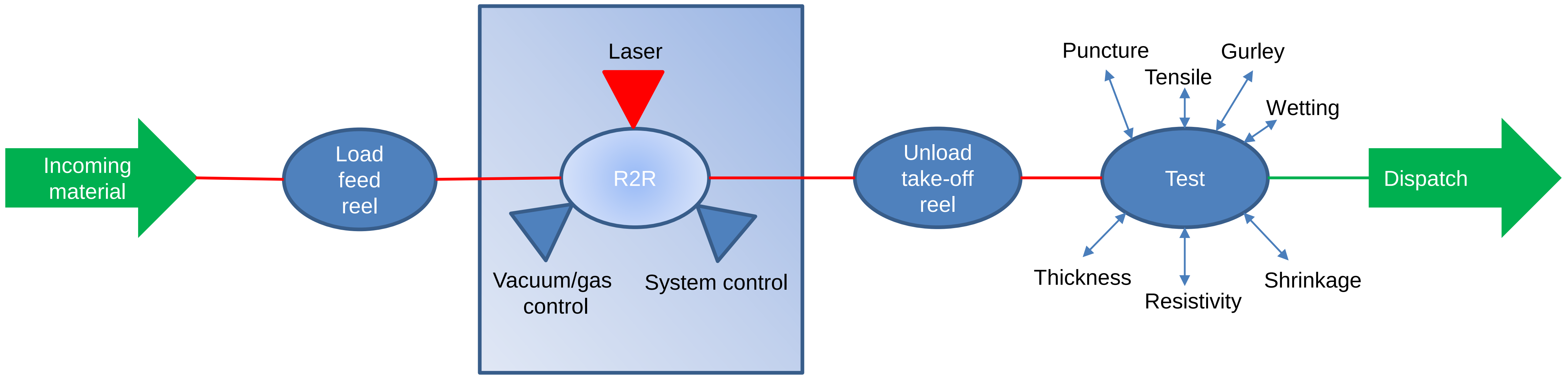
The removed material transfers to a target material where it is deposited

The method employs high power pico or femto second pulse lasers

PLD is useful for coating fragile, temperature sensitive materials such as LIB separators

Picodeon are developing a R2R deposition method suitable for application in a battery manufacturing environment where semi-continuous, high volume production is key to reducing product cost

Picodeon Process Flow Chart



The process flow is straightforward

Process parameters	Reel width 100cm
	Line speed 10m per min
	Minimum runtime 80%
	Annual production 4,200,000 m^2 per year

Competing LIB Separator Coating Technology Comparison

	Picodeon PLD	Slurry	PVD	ALD	CVD
Adhesion	Excellent	Poor	Med	Med	Med
Thermal Budget	Low	Low	Med	Med	High
Stoichiometry Transfer	Excellent	Good	Good	Med	Med
Porosity Control	Good	Good	Poor	Poor	Poor
Cost	Low	Low	High	High	High
Scalability to smaller geometries	Good	Poor	Good	Good	Good

Advantages of Picodeon PLD coated separators

Picodeon PLD can apply the ceramic coating as a dense or porous layer

Thinner coatings down to < 20nm are readily achieved

Increased coating adhesion over slurry coated separator without the need for binders

Highly uniform coatings are possible

Tailored particle size

No solvent or water removal - dry coating method

All the above have either direct impact to increase cell capacity or lead to improved manufacturing processes and potentially reduced scrap rate on the production floor.

Separator impact on battery performance

Separator is an inert component and should not impede the cell functioning

Volume available for active materials – thinner separator = more anode and cathode

Internal resistance of the cell – lower resistance = higher running voltage and lower heating from ohmic losses

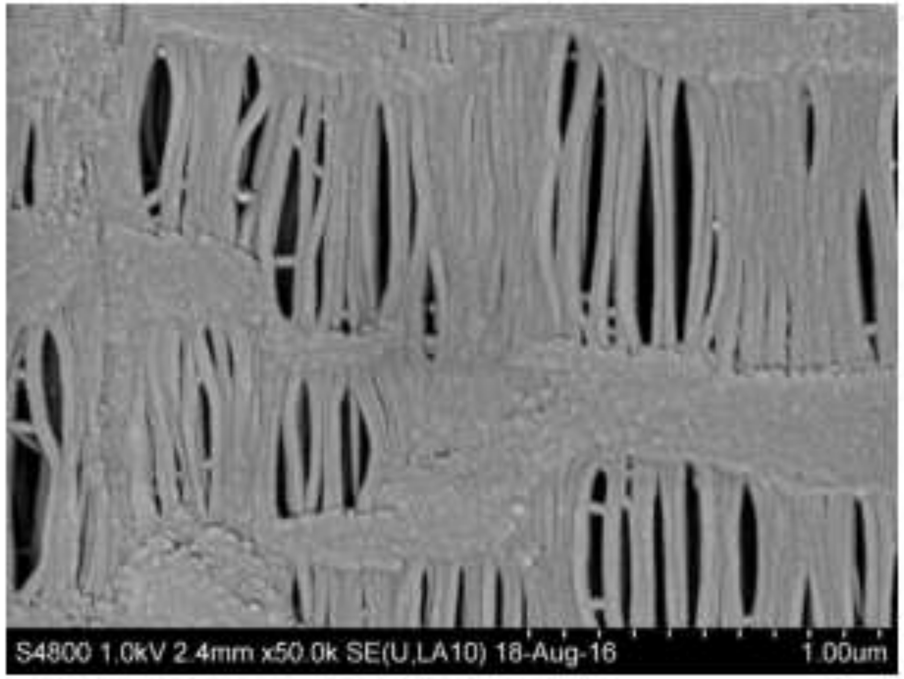
Electrochemical oxidation resistance – separator should not degrade in the cell due to charge/discharge reactions or chemical reactions over time – up to 10 years in EV applications

Ceramic coating can enhance:
- Thermal stability – reduced shrinkage
- Oxidation resistance – a pathway to 5V technology
- Wettability
- Electrolyte retention at the electrode interface
- Puncture resistance

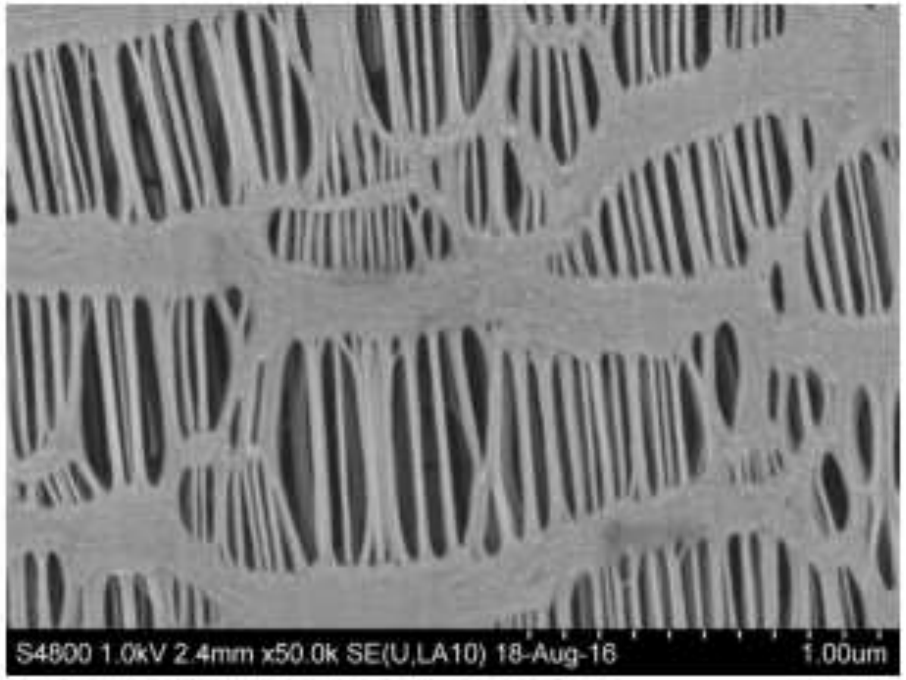
SEM of Picodeon PLD Coated Separators

Dense 20nm thick coating Separator A

Coated

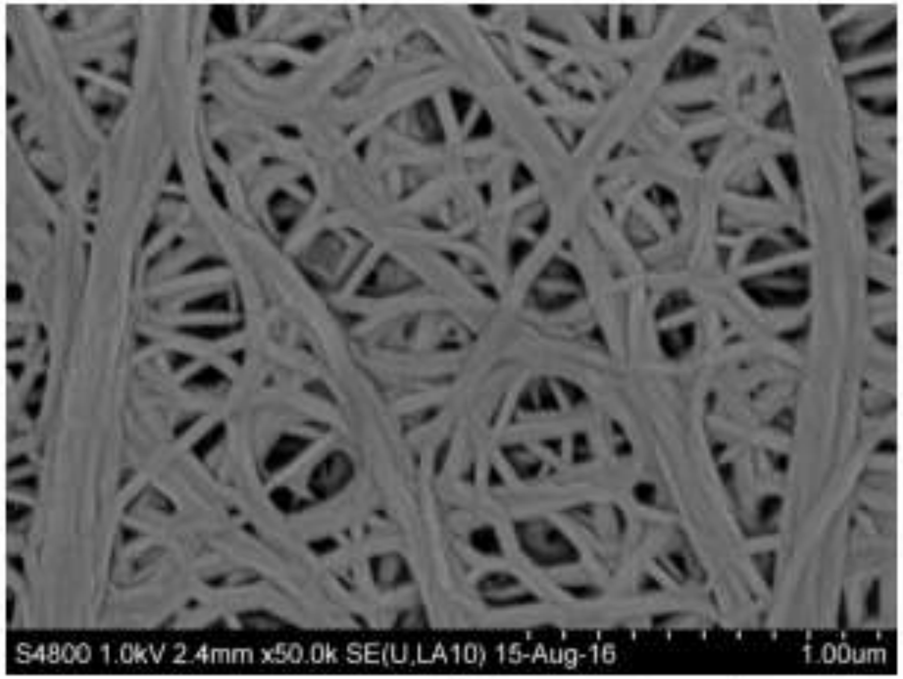


No coating

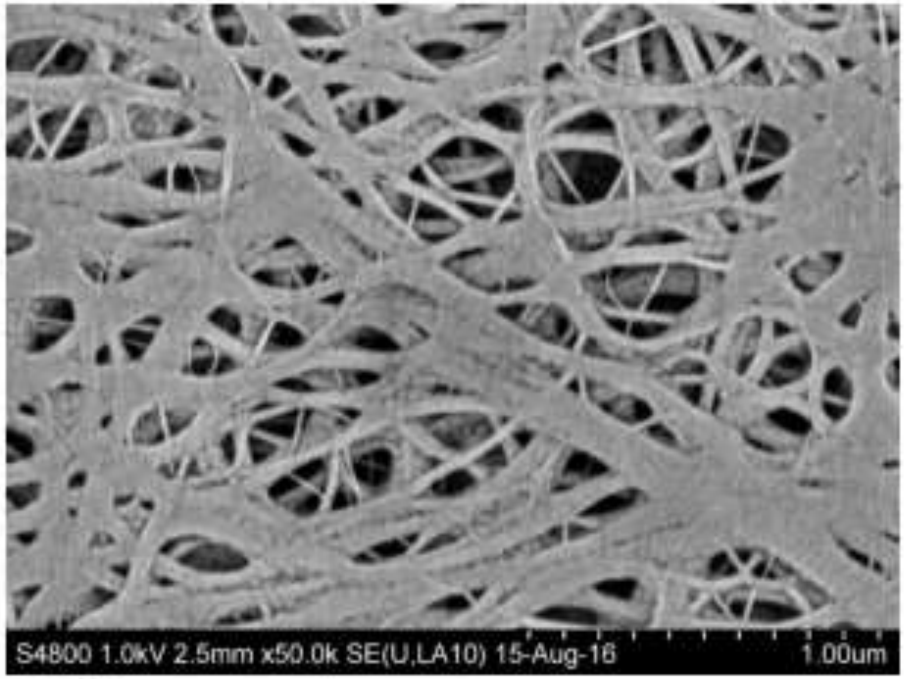


Dense 20nm thick coating Separator B

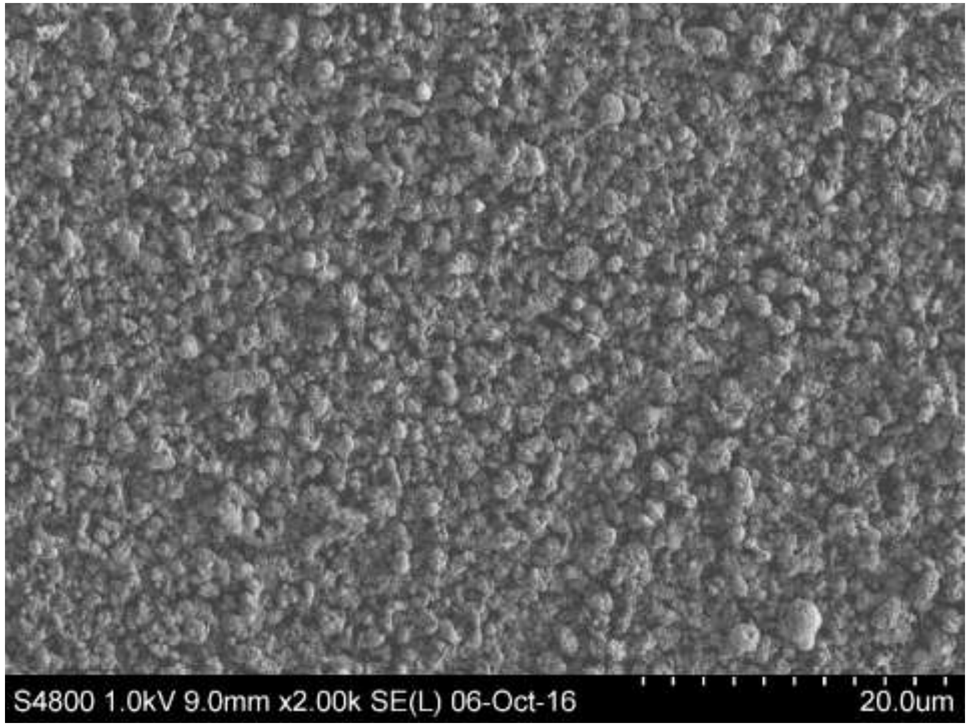
Coated

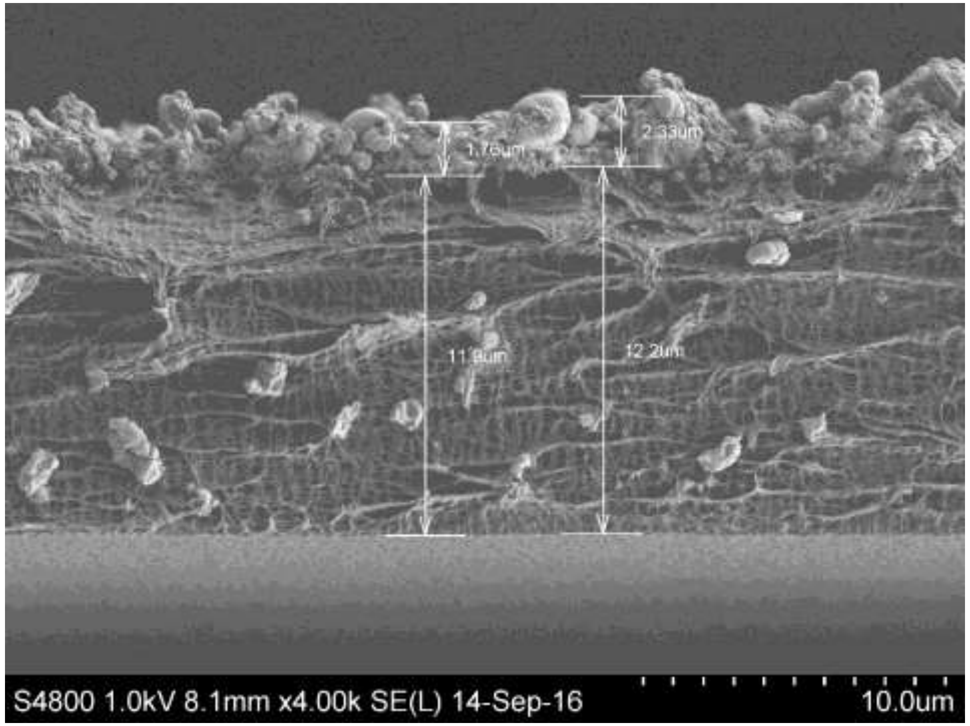


No coating



Porous Coating - 2µ





In-House Testing of coated separators

Visual: no visible damage (melting, wrinkling, etc.) from deposition

Shrinkage: machine direction (MD) shrinkage reduced from baseline, transverse direction (TD) shrinkage is zero at 105 °C

Wettability: rapid wetting in comparison to uncoated reference

Gurley: (Air permeability) porous coating increases Gurley less than 100%

SEM: uniform coating with no damage, desired thickness on cross-section

Resistivity `

Tensile testing

Results: Wettability, Gurley air permeability

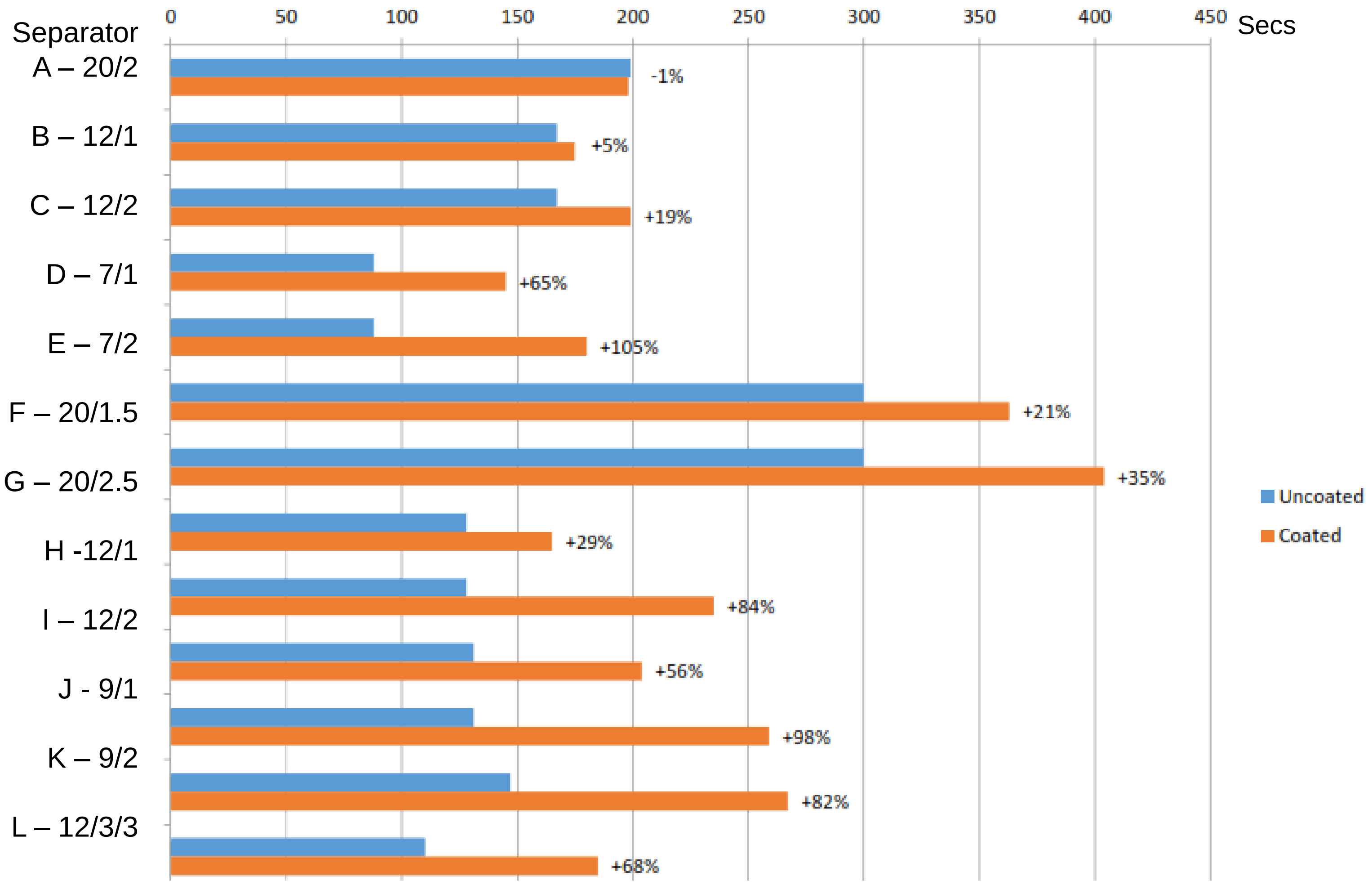
Gurley increased max. 105% with porous coating up to 3µ thick

Largest increase on thin PE membranes and 2-sided coatings

Wettability is excellent on all porous coatings

Wettability Video

Gurley Air Permeability



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Thermal Free Shrinkage tests

Protocols are chosen based on membrane material coating thickness or customer preference

Current protocols: 90/60, 105/60, 130/30, 130/120, 150/30 and 150/120 min, free shrinkage in MD and TD

Good shrinkage performance with > 1 µm porous coating at 130 ºC (both MD and TD)

150 ºC performance can be good, but requires thick (>2 µm) or two-sided porous coating

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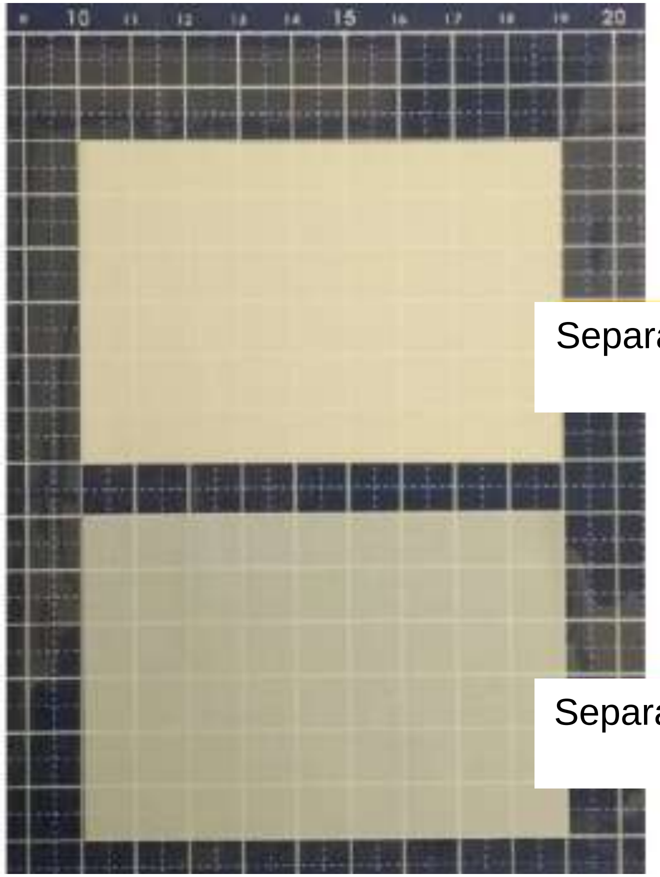
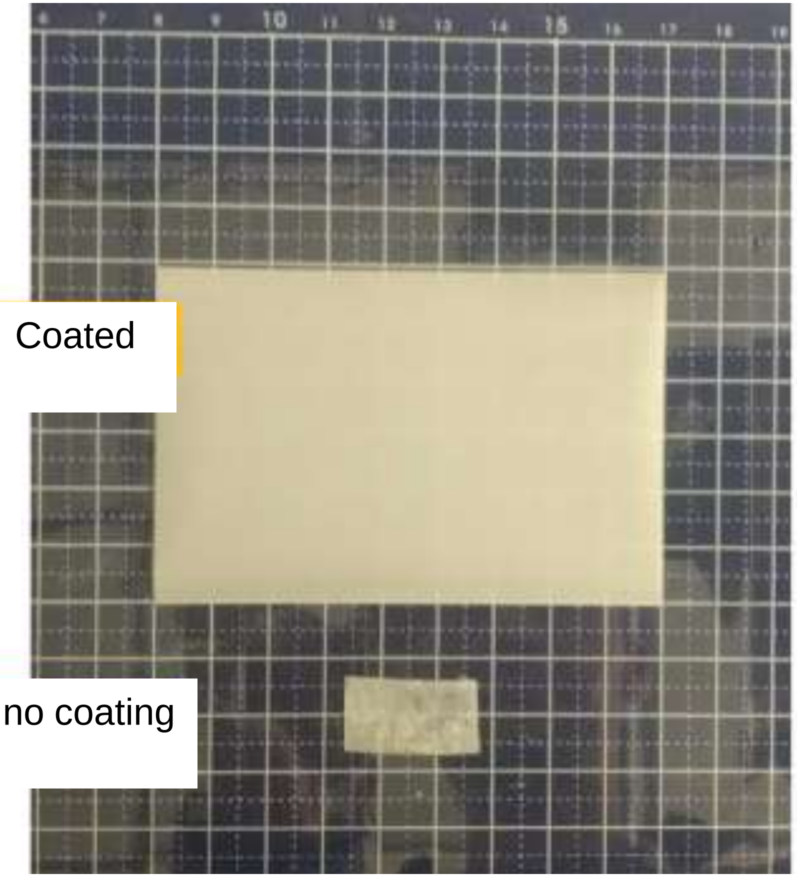
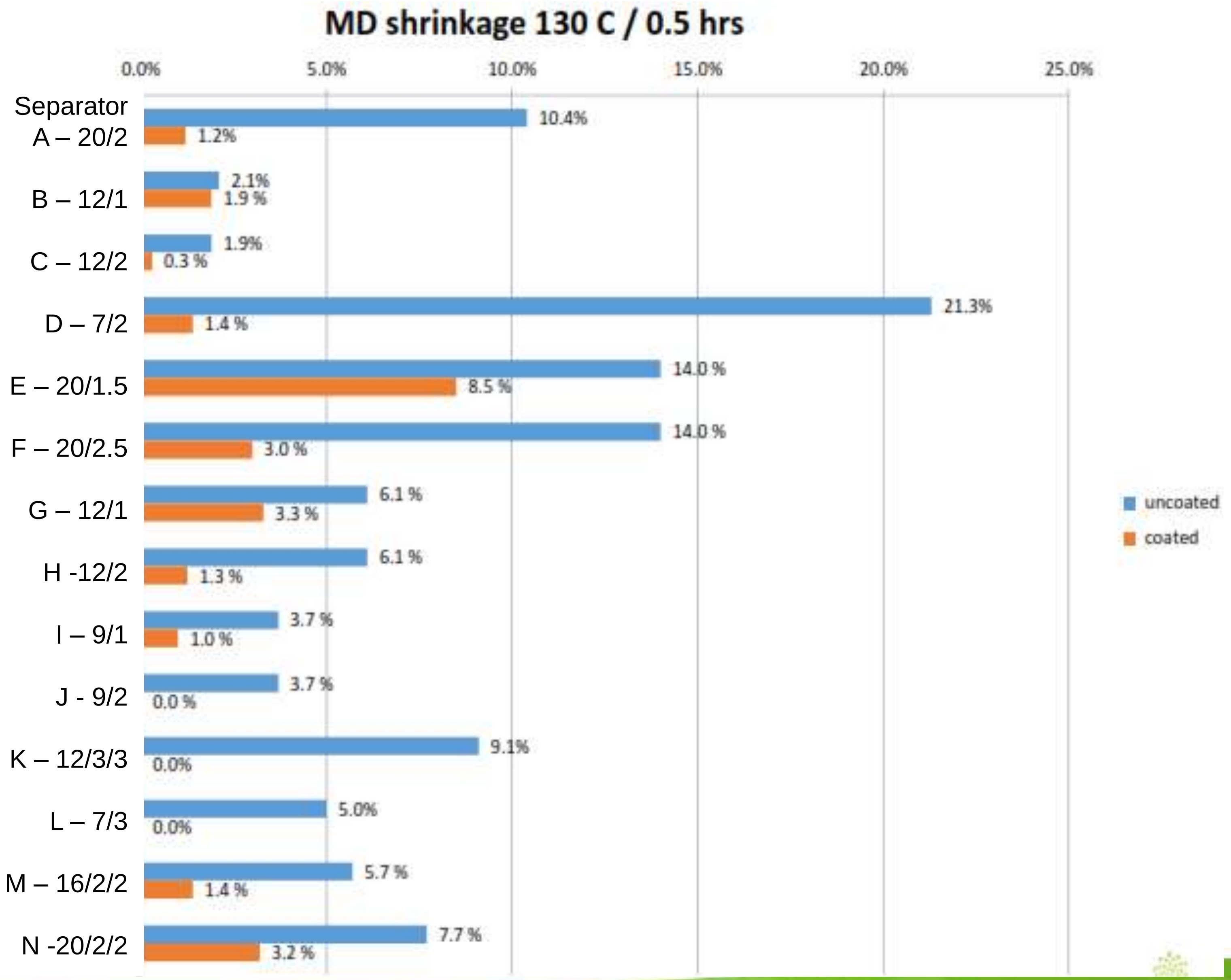
Typical Free Shrinkage Test Result



Separator Coated

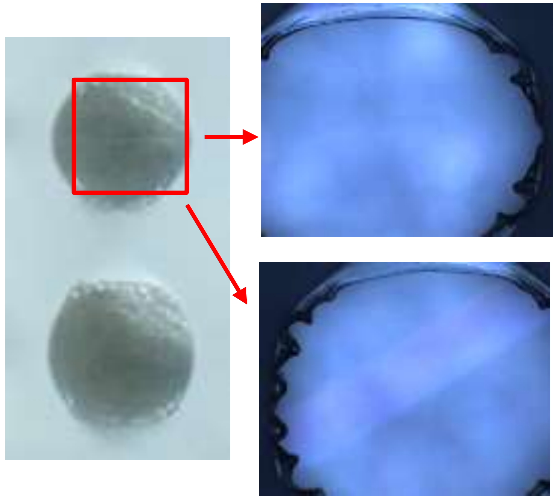
Separator no coating




MD shrinkage 130 C / 0.5 hrs
0.0%
5.0%
10.0%
15.0%
20.0%
25.0%
Separator A – 20/2
10.4%
1.2%
B – 12/1
2.1%
1.9 %
C – 12/2
1.9%
0.3 %
D – 7/2
21.3%
1.4 %
E – 20/1.5
14.0 %
8.5 %
F – 20/2.5
14.0 %
3.0 %
G – 12/1
6.1 %
3.3 %
H -12/2
6.1 %
1.3 %
I – 9/1
3.7 %
1.0 %
J - 9/2
3.7 %
0.0 %
K – 12/3/3
9.1%
0.0%
L – 7/3
5.0%
0.0%
M – 16/2/2
5.7 %
1.4 %
N -20/2/2
7.7 %
3.2 %
uncoated
coated

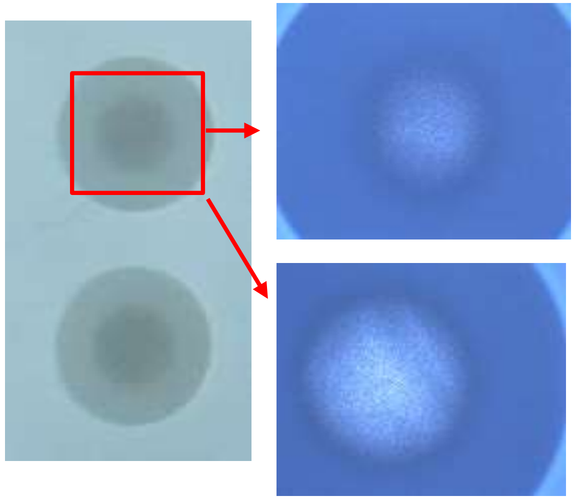
Typical Hot Tip Test

Uncoated



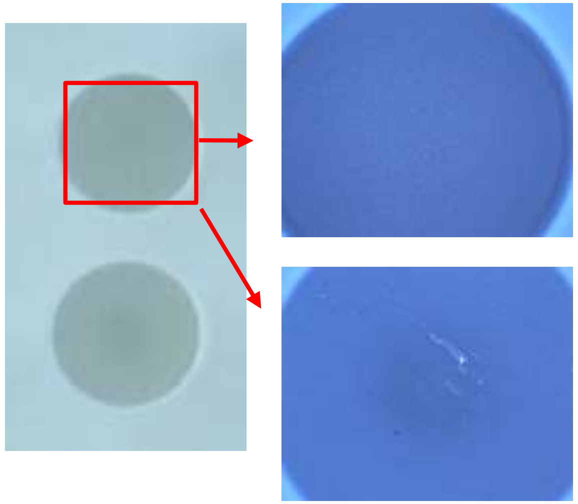
Holes: 2.5-2.9mm
Contact : None

2 um single side coated



Holes: None
Contact: Yes
Colour: Light 2.7-2.9mm
Colour: Dark 0.8-1.3mm

2 um double side coated



Holes: None
Contact: Yes
Colour: Light 2.7mm

250°C for 5 sec, tip diameter 1.8 mm

Testing to be completed in-House

Electrical resistivity – McMullen Number

Tensile properties

Puncture strength

LIB customer cell discharge testing

Discharge data as a percentage of Reference uncoated Separator

Separator	Cycle	20nm	1	2	3
1	1	101	101	100	100
	120	100	101	100	100
2	10	100	-	-	-
	200	100	-	-	-
3	50	-	-	100	-
	200	-	-	100	-

Summary

PLD can be used to coat LIB separators with ceramic materials

PLD can produce thin dense and thick porous coatings

PLD coated separators exhibit excellent wetting with little decrease in air permeability

Thermal shrinkage data is good

Initial discharge data carried out by potential customers is good

Next steps

On-going customer testing and evaluation

Refinement of the laser and control systems

Continued development of the R2R process and production scale equipment

Acknowledgements

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