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Spatial ALD in porous substrates

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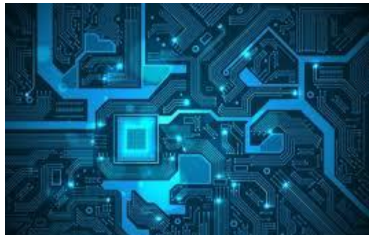
Introduction | SparkNano

SparkNano is a Spatial ALD equipment company, located in Eindhoven, the Netherlands.

We develop and sell high-throughput **Spatial Atomic Layer Deposition equipment**

We focus on applications in **Energy**, **Electronics** and **Optics**



We provide **R&D** and **mass-production** equipment (Wafer / Sheet-to-Sheet and Roll-to-Roll)

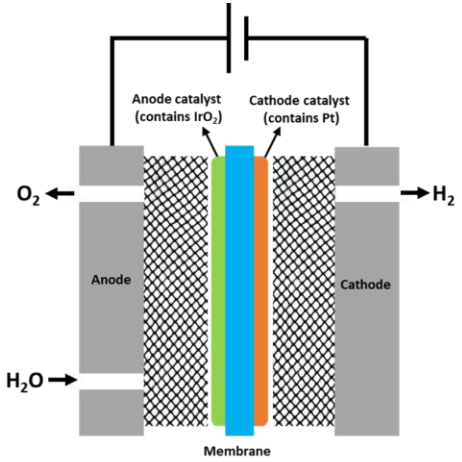
Sheet-to-sheet
← **LabLine** (R&D, up to 30 cm x 40 cm)
← **Vellum** (Mass production, 65 cm x 180 cm)

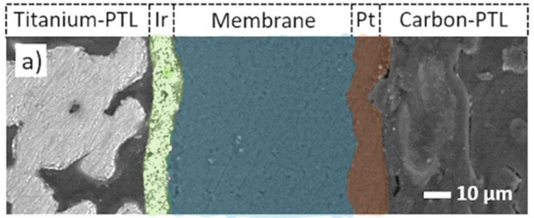
Roll-to-Roll
Omega →
Up to 100 m/min
and 1.5 m wide

Introduction | Examples of applications: Green H_2

Water electrolysis and fuels cells

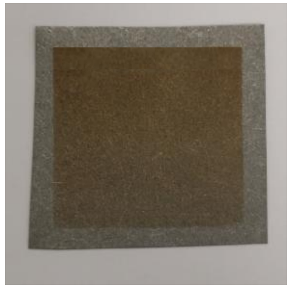
- PEM water electrolysis is used to produce green H_2 from water and electricity
- But: rare and expensive catalysts like Ir and Pt are used
- The use of these materials should be reduced significantly to make PEM electrolysis viable



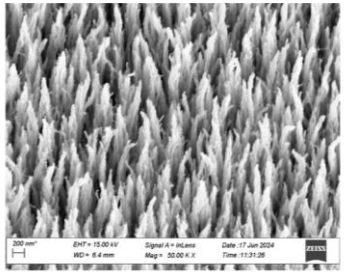


Adapted from: Bernt et al, J. Electrchem. Soc. 165 (2018) F305

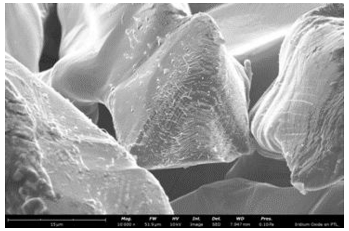
- Using Spatial ALD it is possible to apply conformal coatings on porous and high surface area supports
- **The use of Ir and Pt can be reduced 10-100x!**



Electrolyzer electrode



Pt-coated fibers



IrO_2-coated fibers

- Main challenges: deposition in porous substrates, using very expensive precursors
  Efficiency is paramount!

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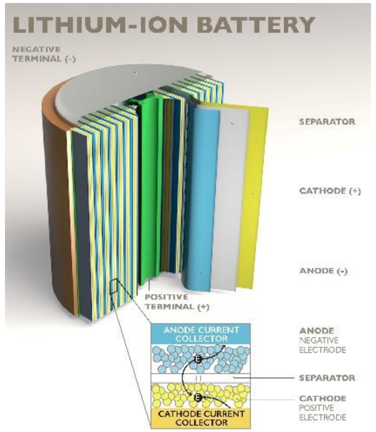
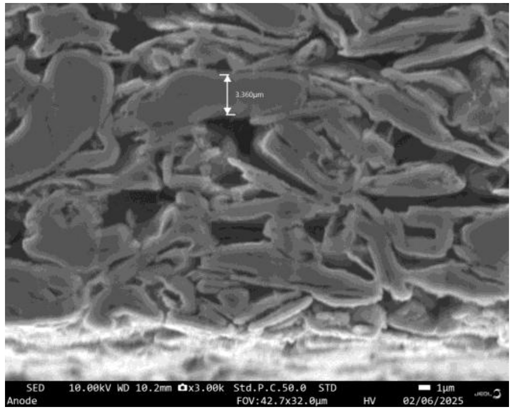
Introduction| Examples of applications: Li-ion batteries

Li-ion batteries

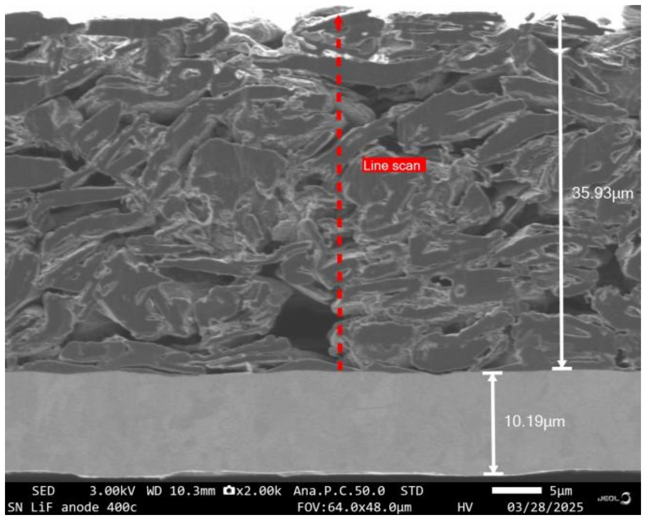
- Spatial ALD of “passivation layers” on battery electrodes, improving capacity and lifetime
  - Materials: metal oxides and fluorides

- Main challenges: Up-scaling; deposition in porous electrodes at very high throughput numbers
- **Precursor flows of 100’s grams/hr are required!**

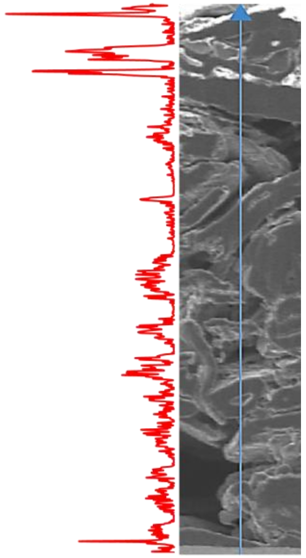




- Example: **conformal LiF coating inside a graphite anode**
  - Fluorine signal by EDS, from top to bottom



Graphite anode with conformal LiF coating



EDS line scan for F

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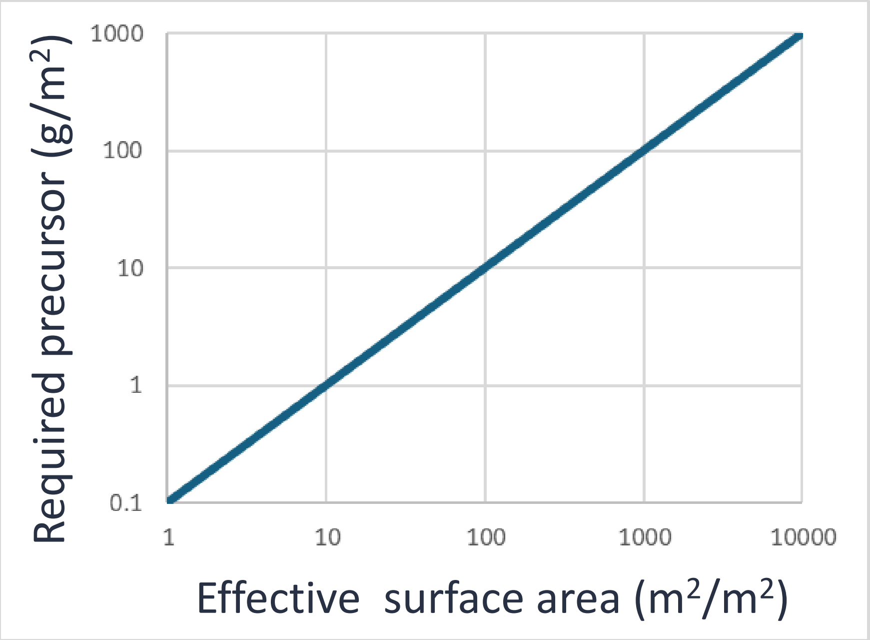
Introduction | ALD in porous substrates

- **Scaling up ALD for porous and 3D substrates** is of tremendous importance for many applications in electronics, energy and catalysis

- Porosity leads to an increase in **effective surface area**
  - 10's-100's m^2/m^2 (electrodes) - 1000's m^2/m^2 (e.g. CNT's)

- The amount of precursor that needs to be supplied **scales with substrate area**

- How to avoid **throughput limitations** due to insufficient precursor supply?
- How to avoid **high precursor cost** due to overdosing?

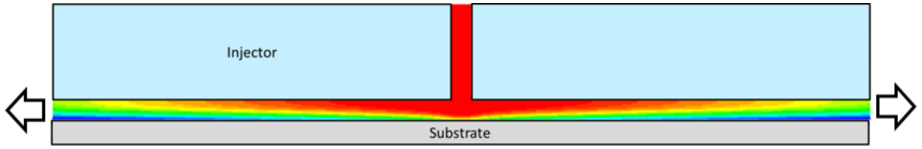


Introduction | Precursor efficiency

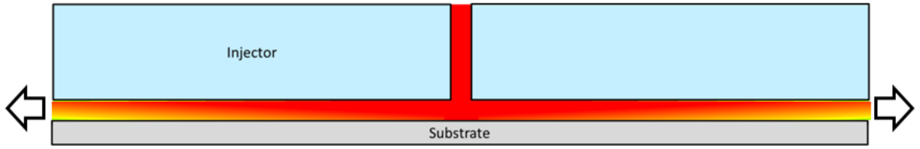
- A key parameter in optimizing precursor dosing is the **precursor efficiency η**

$$\eta = \frac{\text{Amount of precursor that ends up in the film}}{\text{Amount of precursor supplied}}$$

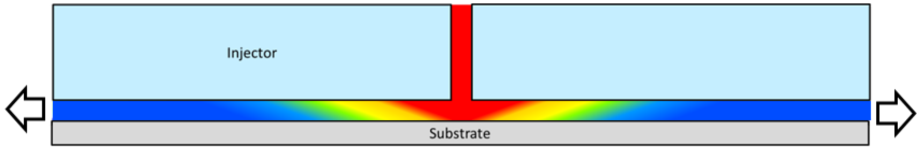
- Optimizing the efficiency is finding a delicate balance
  - Precursor reactivity (e.g. sticking coefficient)
  - Substrate size, porosity and reactivity
  - Precursor transport by gas flows and diffusion
  - Substrate speed, Spatial ALD head design, gap height, …..
  - Throughput- and deposition rate targets



Balanced precursor efficiency and deposition rate

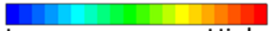


Low precursor efficiency, high deposition rate



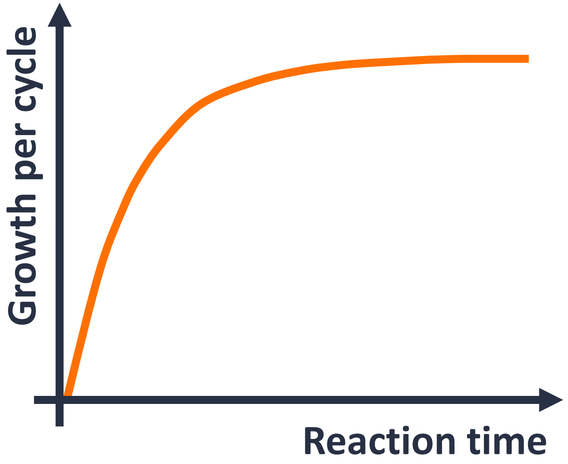
High precursor efficiency, low deposition rate

Precursor concentration



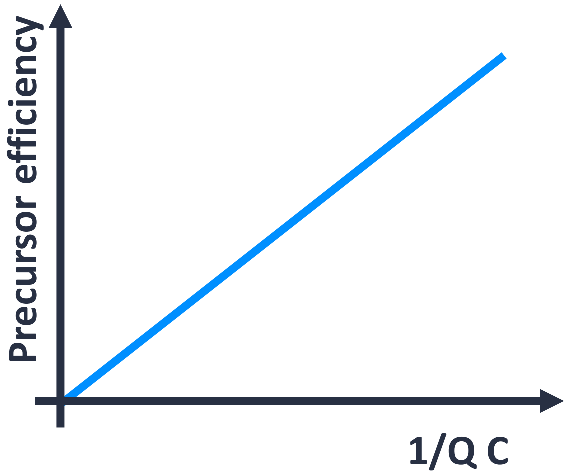
Introduction | Maximizing precursor efficiency

- The precursor flow (F_r) required for a monolayer: $F_r \propto \frac{GPC\ A}{t}$
  - GPC = growth-per-cycle (nm)
  - A = substrate area (m^2)
  - t = reaction time (s)



- The supplied precursor flow: $F_s = Q\ C$
  - Q = total gas flow (m^3/s)
  - C = precursor concentration ($\#/m^3$)

- Precursor efficiency: $\boldsymbol{\eta = \frac{F_r}{F_s} \propto \frac{GPC\ A}{Q\ C\ t} \propto \frac{1}{Q\ C}}$



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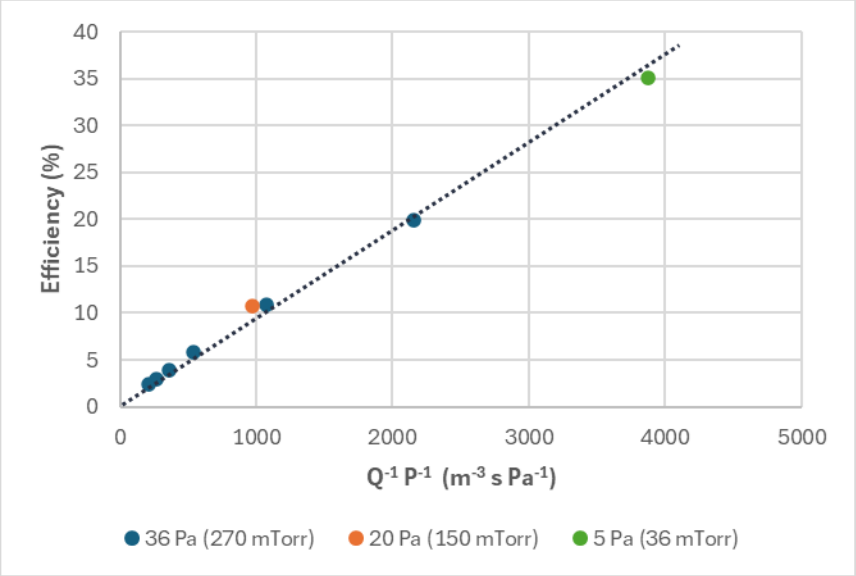
Results | Precursor efficiencies on planar substrates

- As a model system, we investigated **Spatial ALD of Nb_2O_5**
  - SparkNano LabLine R&D tool
  - Nb_2O_5 using Nautilus and H_2O;
  - Nautilus supplied by Air Liquide Advanced Materials
  - Si wafer and 10 cm x 10 cm high surface area CNT substrates
  - Nb-loading measured with SE, XRF and an analytical balance

- With these conditions, a precursor efficiency of **~35%** has been achieved
  - The efficiency can be further increased, but the GPC will decrease
- **For porous substrates, the situation is very different…**



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Results | Efficiency on high surface area substrates

- **What happens if we use porous and high surface area substrates?**

- We deposited Nb_2O_5 on a 10 cm x 10 cm porous, high surface area substrate

	Si wafer	High surface area porous substrate
Effective area	1 cm^2/cm^2	? (A lot…)
Slope of efficiency vs. $\frac{1}{Q\ C}$	1	64
Precursor mass flow used	1	30
Precursor efficiency reached	35%	**78%**

- On various high surface area substrates, and for various ALD processes,
  75-95% precursor efficiencies can be achieved

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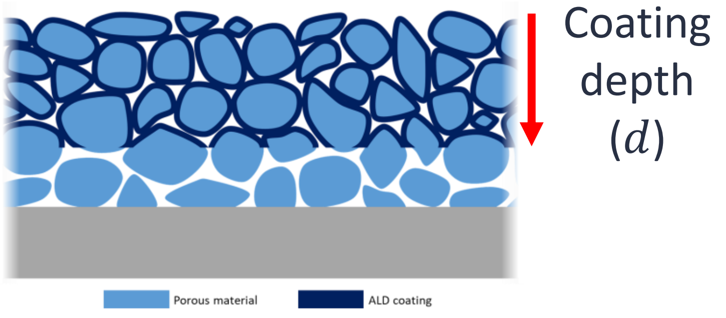
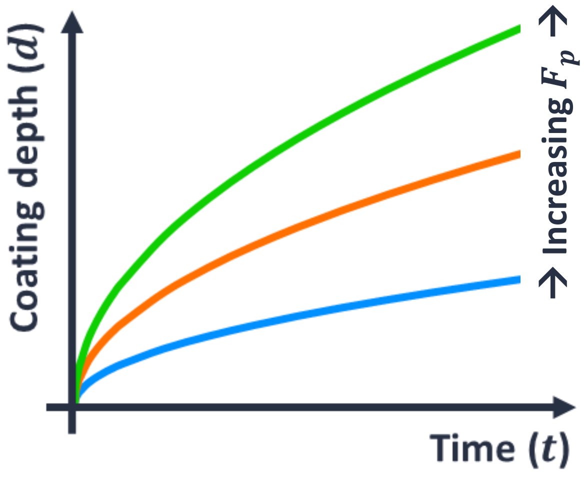
Results | ALD in porous substrates

- To coat inside a porous substrate, the precursor has to creep into the pores
    - This is called diffusion
    - Diffusion is faster when more precursor is available



- To reach a depth d in a given amount of time t, a minimum amount of precursor F_p needs to be supplied:

$$\boldsymbol{F_p \sim \frac{d^2}{t}}$$



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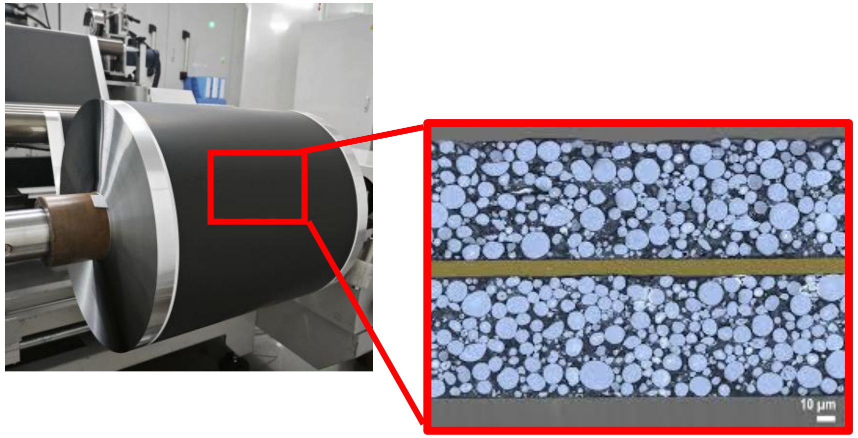
Results | ALD in porous substrates

- Porous substrates often have a large internal surface area

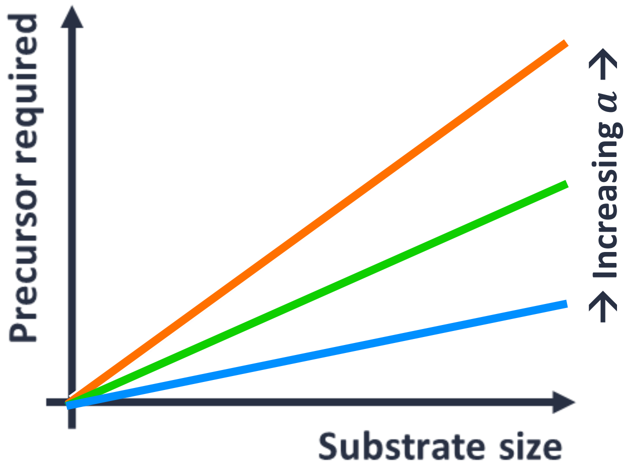
$$A_{internal} = a_{specific} \times A_{geometric}$$

- E.g. the internal surface area of a battery electrode can be 10's-100's times the geometric surface area



- The larger the total coated surface area, the more precursor flow needs to be supplied

$$F \sim \frac{A_{internal}}{t} = \frac{a_{specific} \times L \times W}{t}$$



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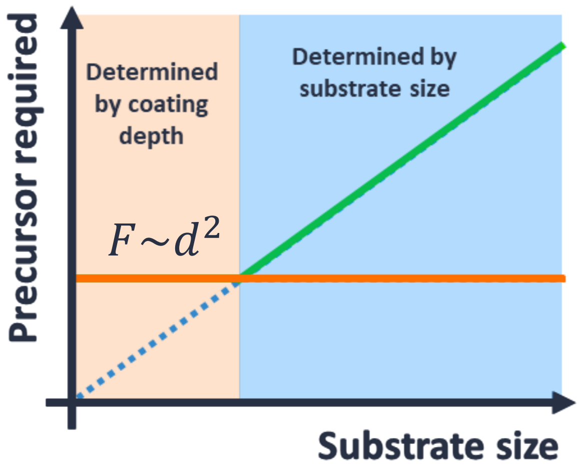
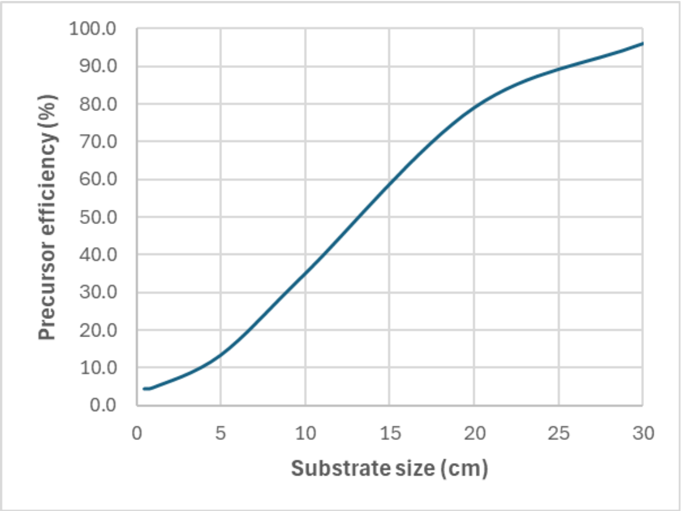
Sustainable ALD | ALD in porous substrates

- For small substrates (~ few cm^2) the total surface area is small and the flow required to reach the required depth is leading
- For larger substrates, the real coated surface area becomes important



- For small substrates with deep pores, a large precursor flow can be required to reach the required depth even if the coated area is still small
  - **Precursor efficiency is low**
- But: if the substrate size increase, the **precursor efficiency increases**



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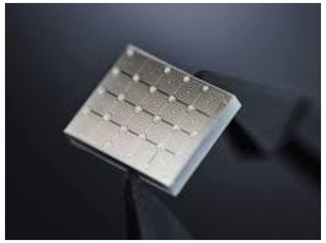
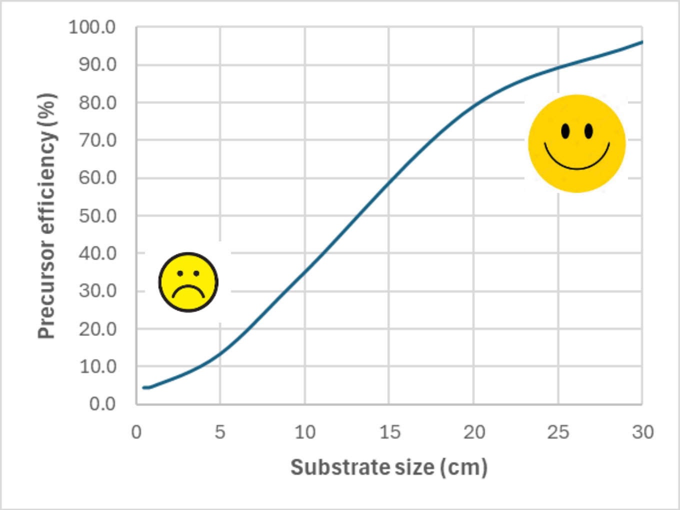
Sustainable ALD | ALD in porous substrates

- Many ALD process optimization studies are performed on small test substrates
  - E.g. AAO’s, coupons with etched structures, coin-cell electrodes…
- However, the effects of surface area only become apparent for larger substrates
- Extrapolating optimization results from small samples can lead to wrong conclusions
- If the goal is to optimize for high volume, **use large substrates** and a **large enough Spatial ALD tool**





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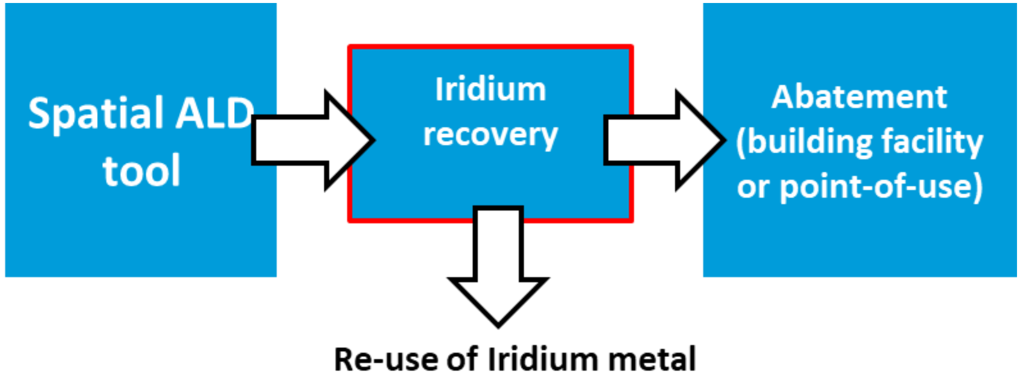
Sustainable ALD | Precursor reclaim



- No ALD reaction is 100% efficient in precursor use. So capturing and re-using e.g. iridium from unreacted precursor is essential
- We are testing solutions to reclaim iridium from unreacted precursor from the ALD reactor waste gas
- Metal reclaim efficiencies up to 90% have been demonstrated
- A pilot-scale reclaim system developed by Air Liquide is being tested on our Labline system

Conclusions| Spatial ALD in porous substrates

- **Scaling up ALD for porous and 3D substrates** is of tremendous importance for many applications in electronics, energy and catalysis
  - E.g. catalyst coated electrodes for electrolysis and fuel cells
  - E.g. passivation of electrodes for high energy density Li-ion batteries

- These applications require **(very) high precursor flows** to match the high surface area involved

- Careful optimization is required to avoid **throughput limitations** due to underdosing and high **precursor cost** due to overdosing

- Precursor efficiencies of **75%-95%** can be achieved on high surface area substrates
- **Precursor reclaim** can be used to further reduce waste

- When doing process development and up-scaling studies: **go big!**

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Thank you for your attention

Reach out to us

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