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Atomic Layer Deposition: Pioneering Research with Atomic- Scale Precision

MIT.nano TOOL TALKS EXPRESS

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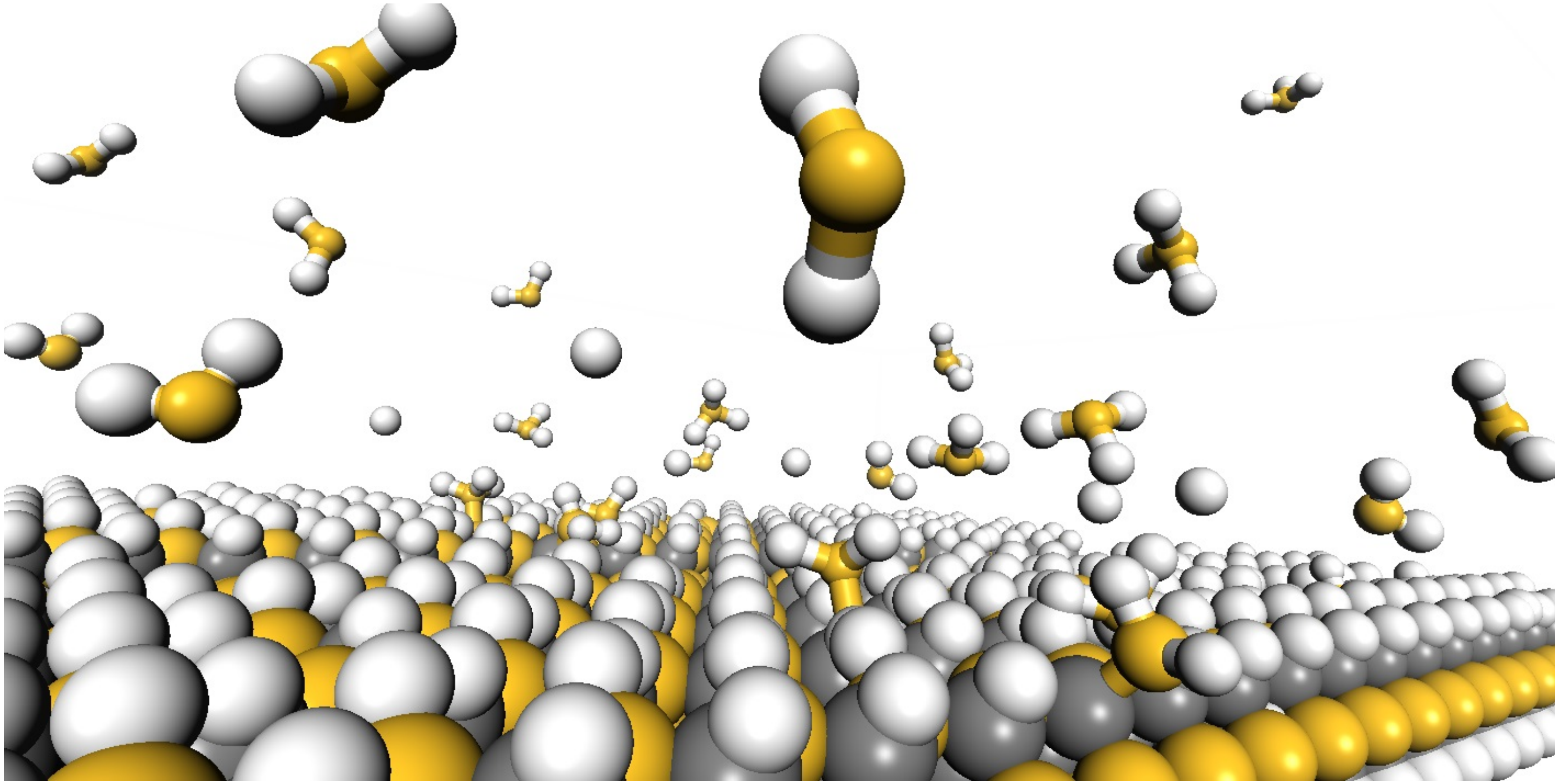
Outline

- Introduction to Atomic Layer Deposition
- ALD - Energy Storage
- ALD- Catalyst Research
- Summary

*All information being presented may be found within the Public Domain

Introduction to Atomic Layer Deposition



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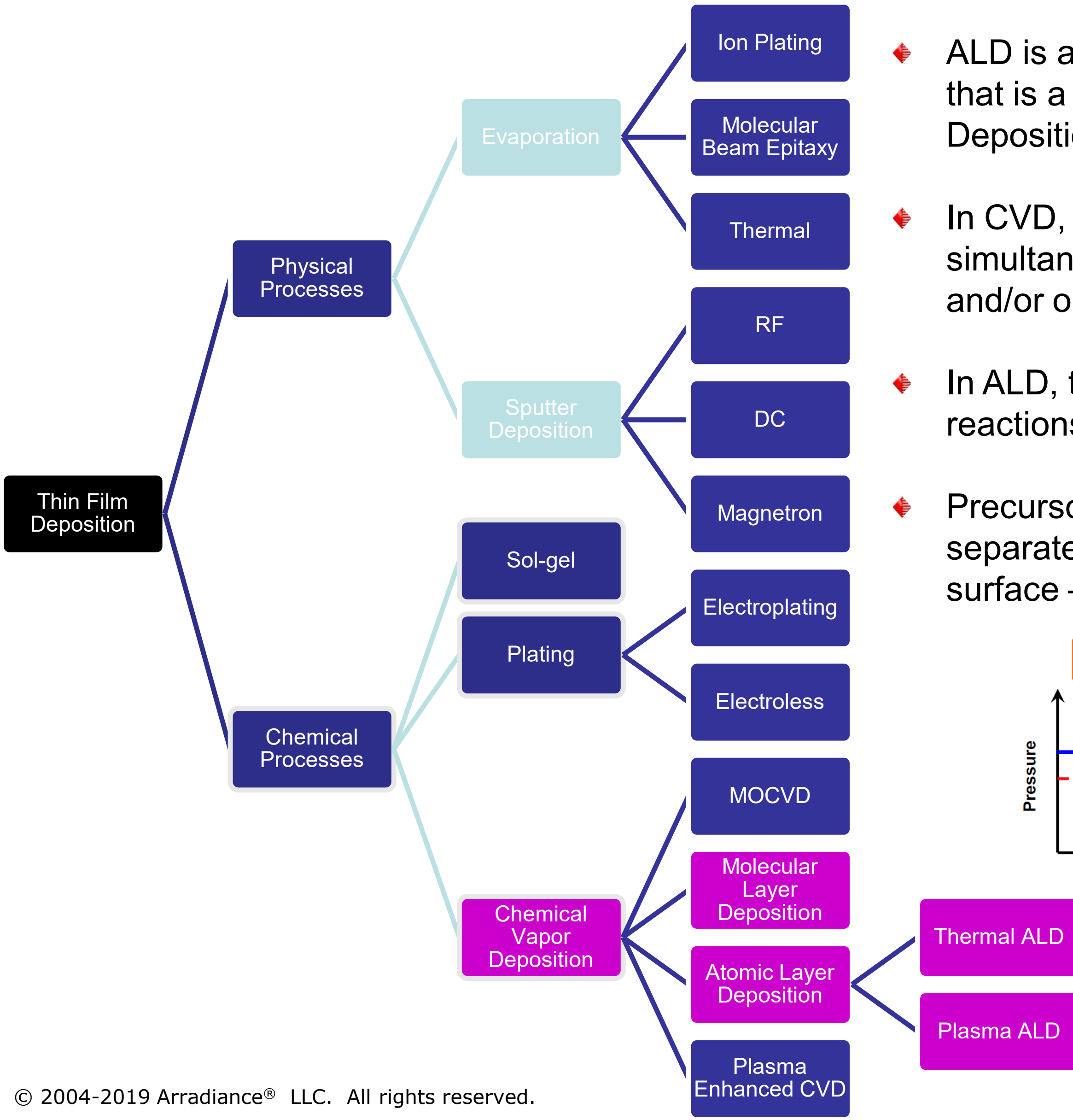
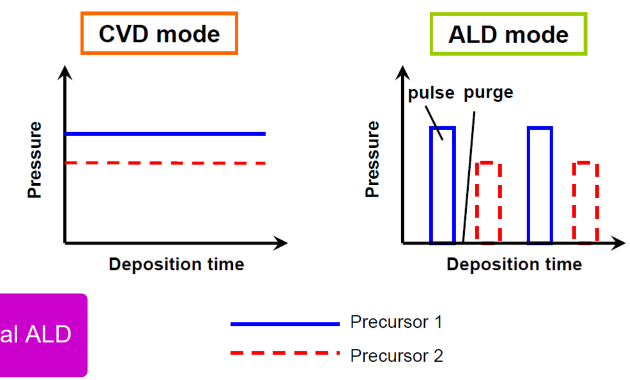
Introduction to ALD – Thin Film Deposition Techniques

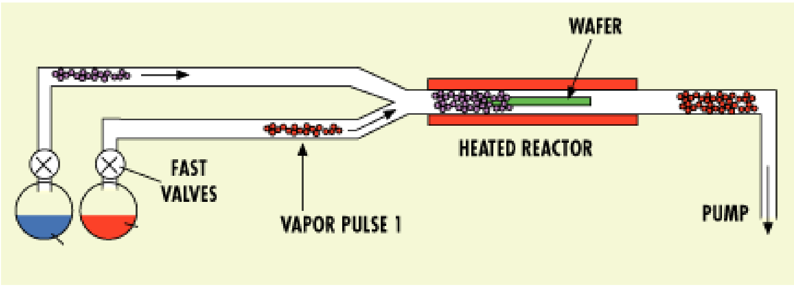


- ALD is a thin film deposition technique that is a subset of Chemical Vapor Deposition
- In CVD, two precursors are introduced simultaneously to react in gas phase and/or on the surface to produce a film
- In ALD, the reaction is split into two half reactions
- Precursor gasses are temporally separated to maximize reaction with the surface – Surface mediated technique

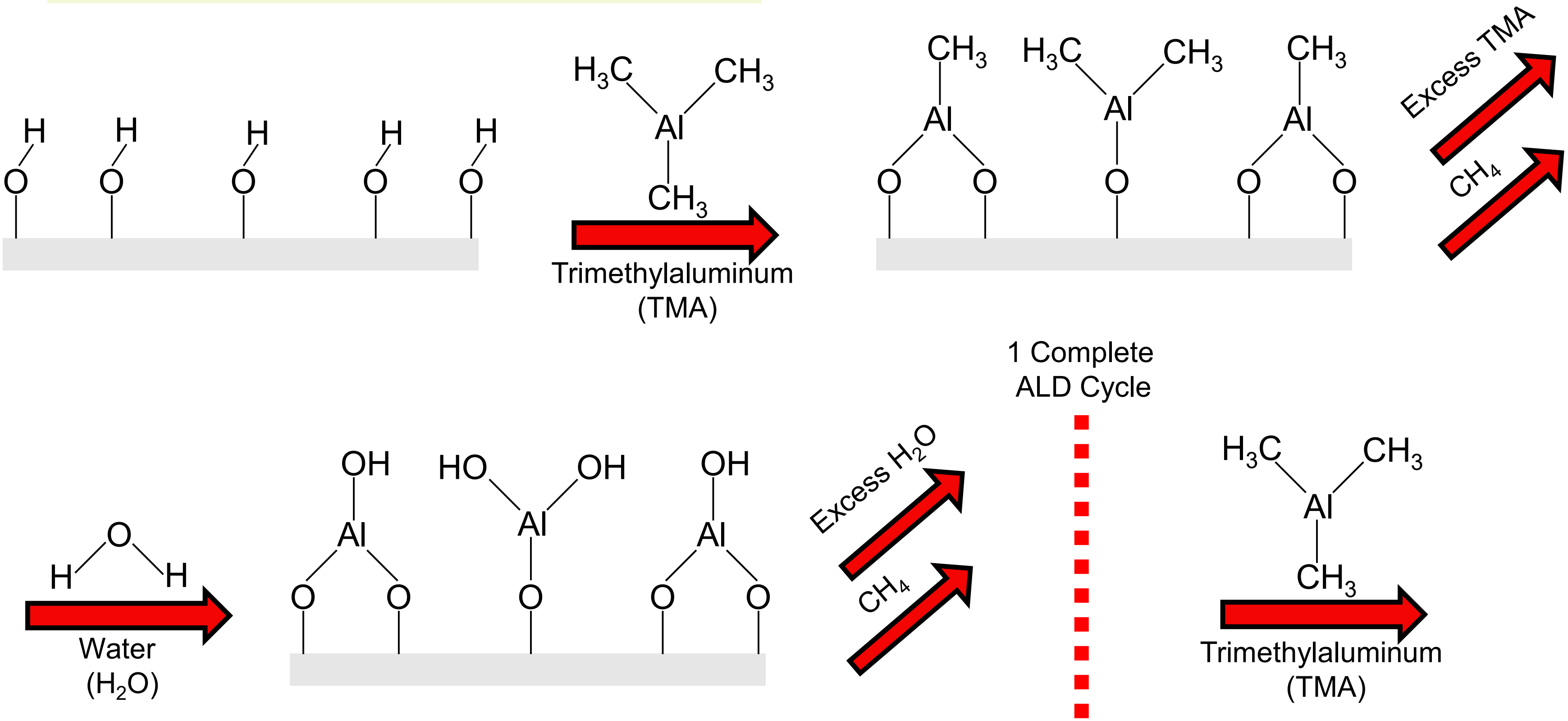


Introduction to ALD – Chemical Reactions

- Simple ALD Design

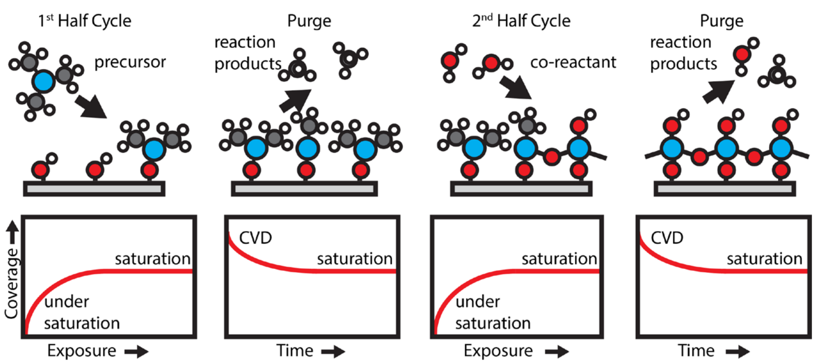


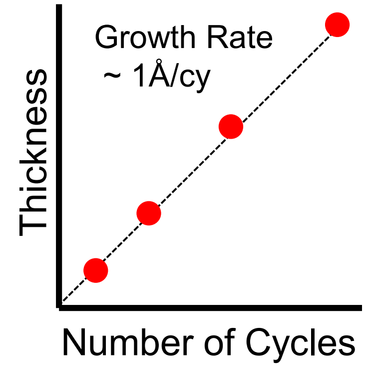
- Surface Mediated Technique – Surface functionality plays an important role
- Examples of ALD: Growth of Aluminum Oxide (Al2O3) using Trimethylaluminum and Water

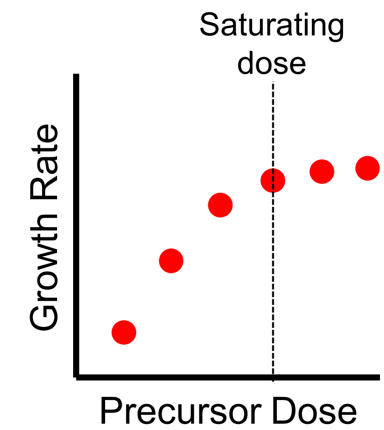


Introduction to ALD – Parameters that Influence ALD

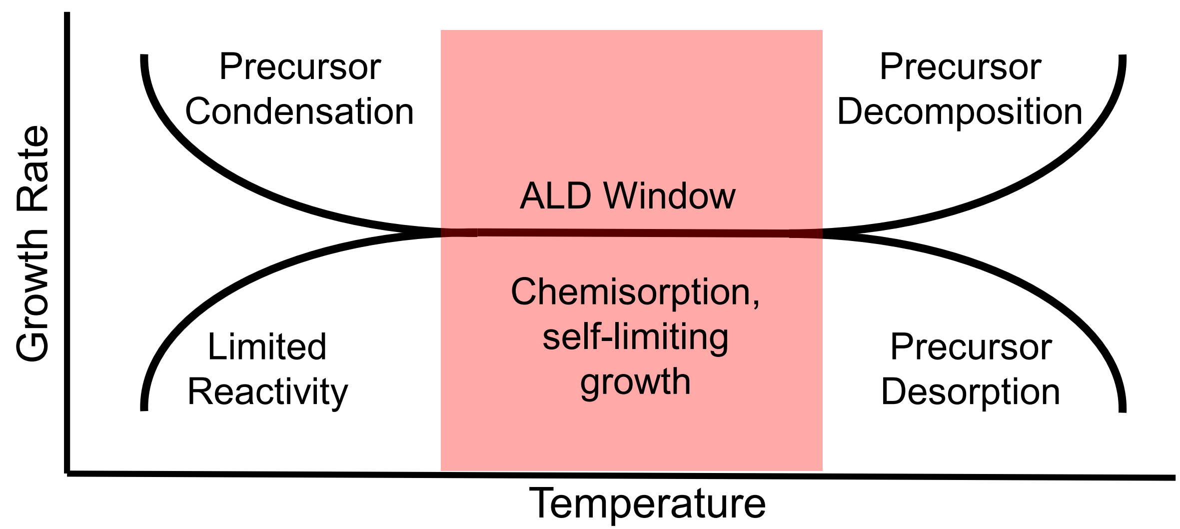
- Surface saturating dose of precursor is required



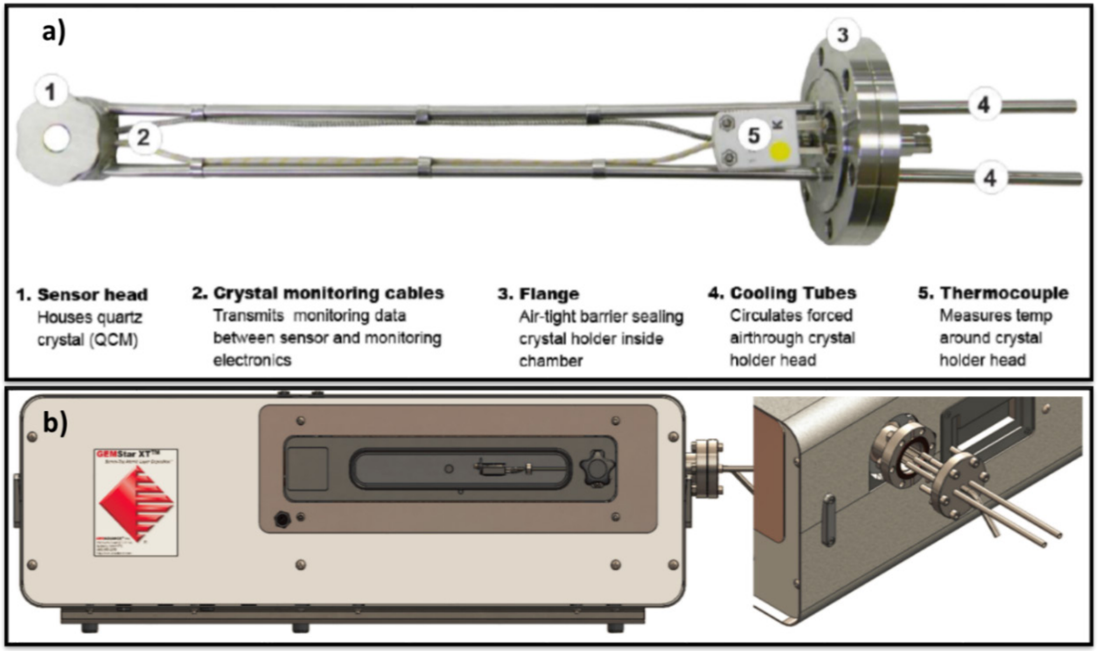




- Reaction temperature to facilitate ALD growth



Using QCM to Monitor Growth



Quartz has a very well defined piezoelectric response.
This can be used to measure mass changes during film growth.

$$\Delta f = -\frac{2f_0^2 \Delta m}{A\sqrt{\mu\rho}} = -C\Delta m$$

Δf = Change in resonant frequency

f_0 =fundamental resonant frequency of the crystal

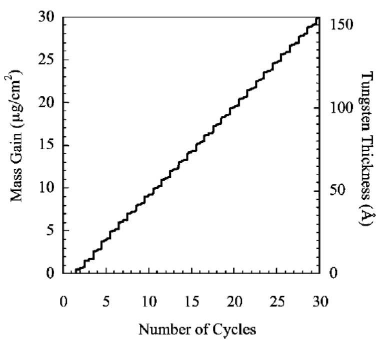
Δm = Change in mass

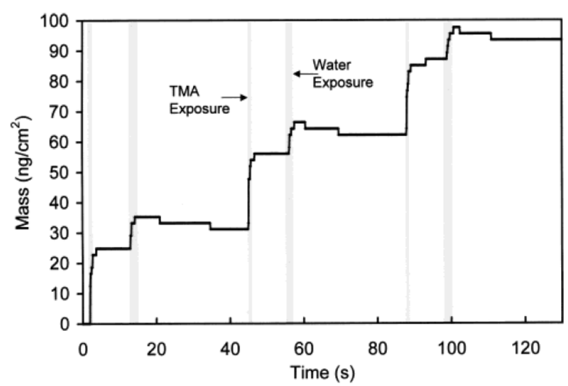
A = Surface area of exposed crystal

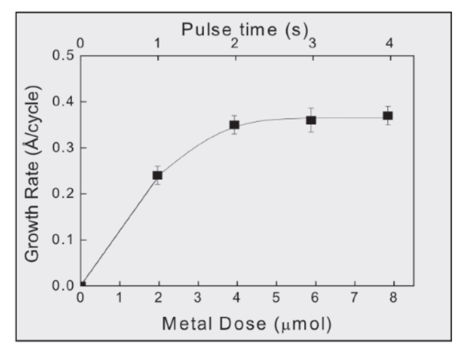
μ = Shear modul of crystal

ρ = density of Quartz

C = Crystal dependent constant

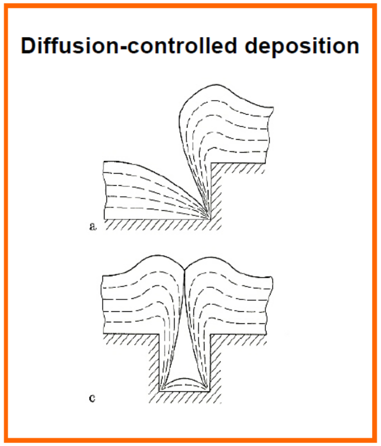


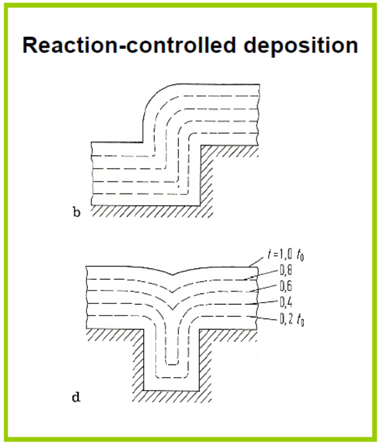


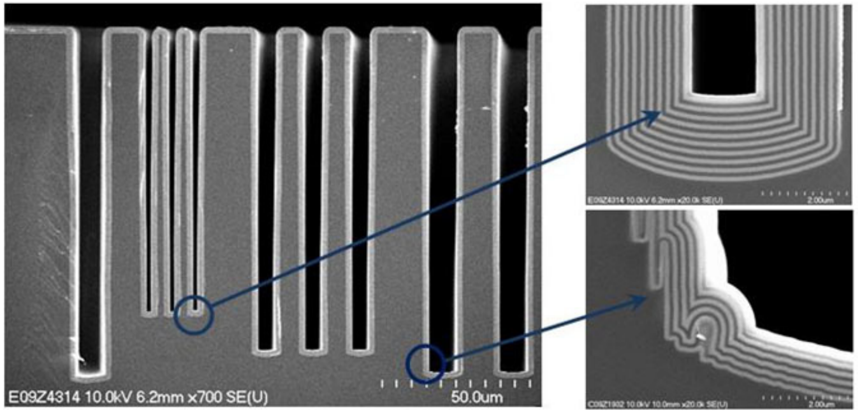


ALD vs Other Gas Phase Deposition Techniques

- ALD is a reaction-controlled deposition technique rather than a diffusion controlled deposition process

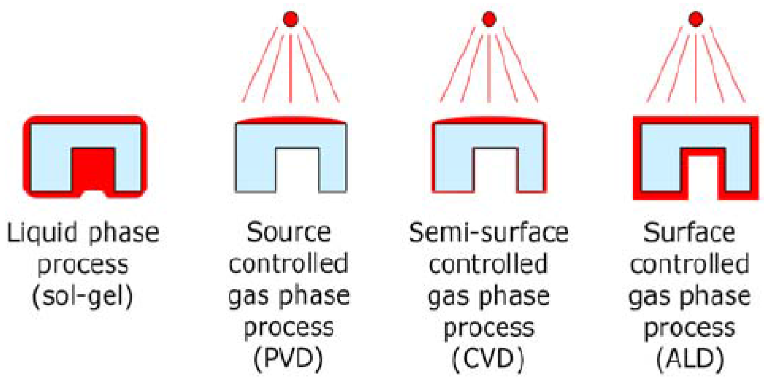


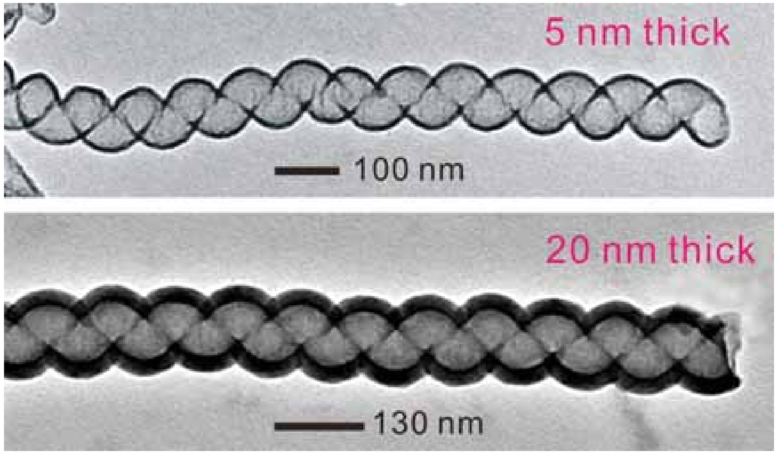




Alternating Layers of Ta2O5 & Al2O3 on deep trenches in silicon

- ALD is also a non-line-of-sight process. Allows for conformal pin-hole deposition around geometrically constrained complex objects





Precursor Chemistry for ALD

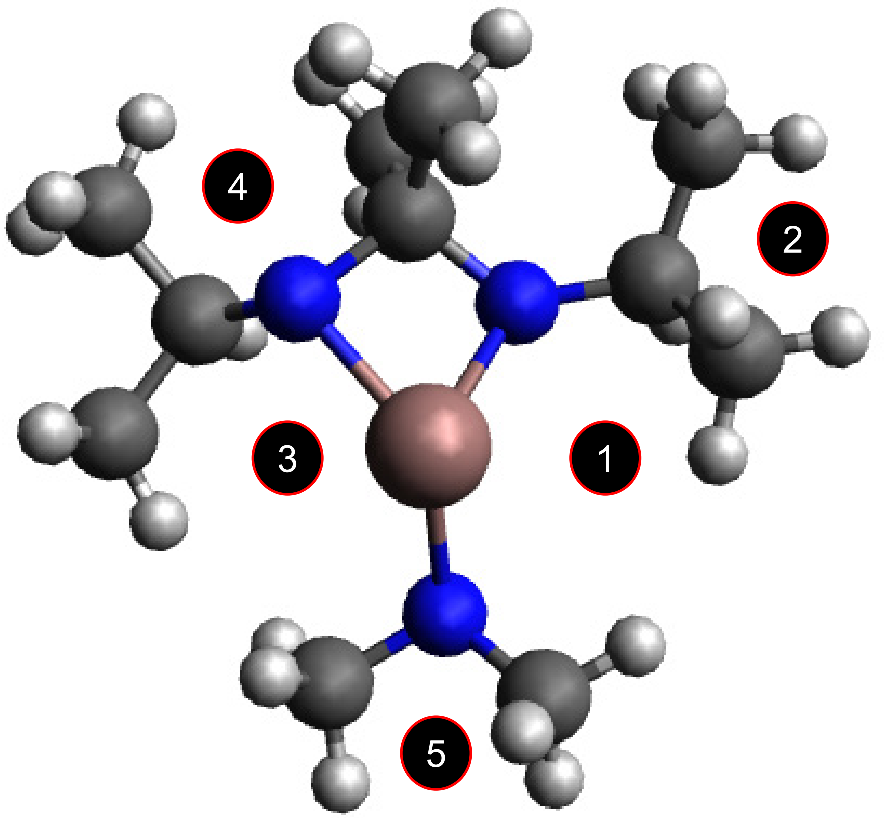
1. Volatile : Coordinatively saturated, low molecular weight

2. Low Melting Point: Branching

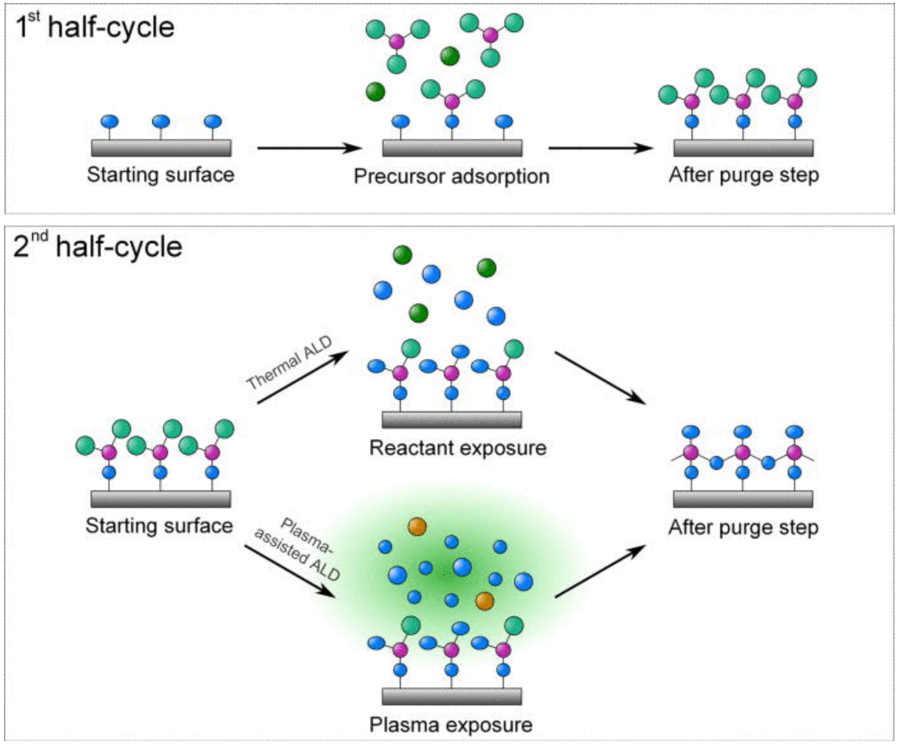
3. Thermally Stable: Strong bonds to metal center

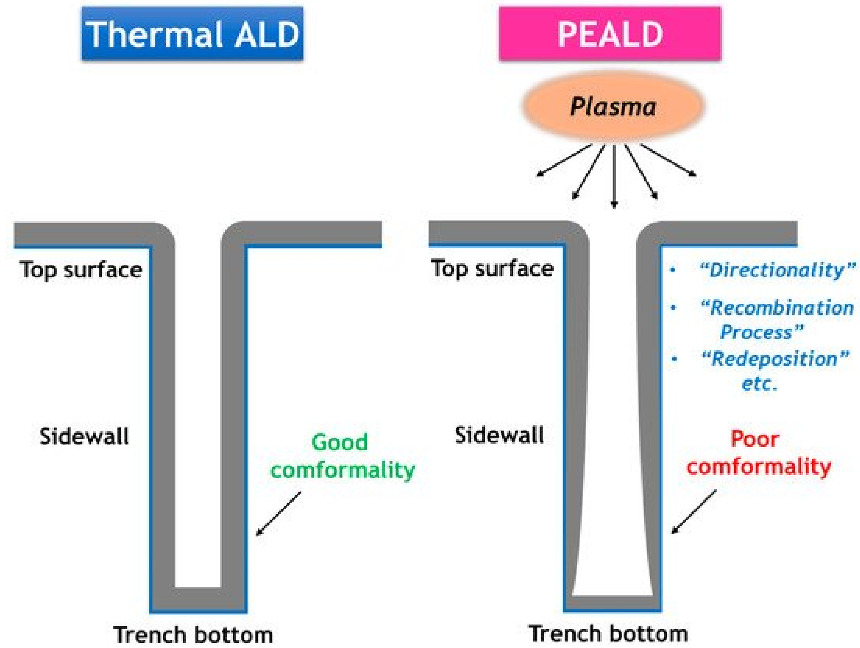
4. Chemically Reactive: bond formed during deposition are strong than those broken

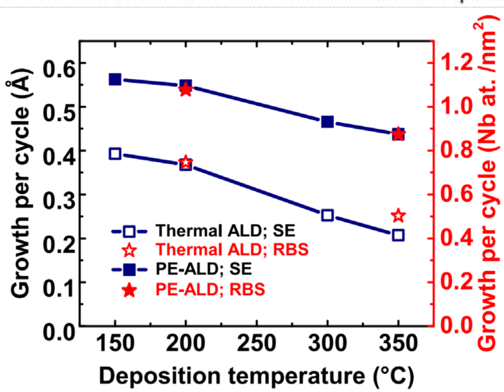
5. Self-limiting Monolayer: steric protection of the central atom keeping it from interacting with other precursor molecules

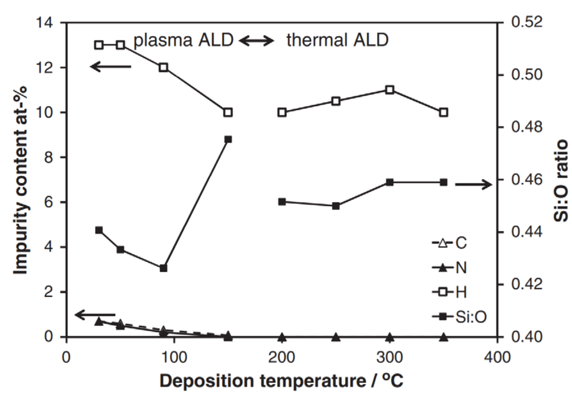


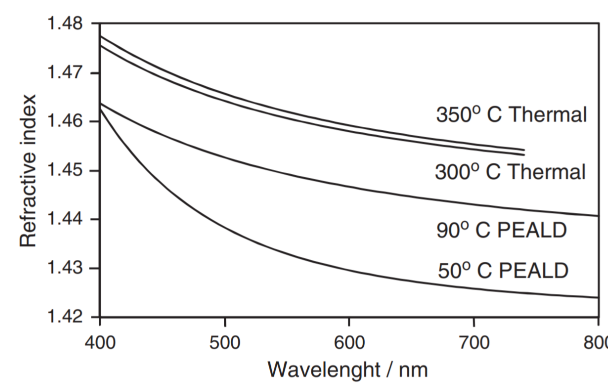
Thermal vs Plasma ALD



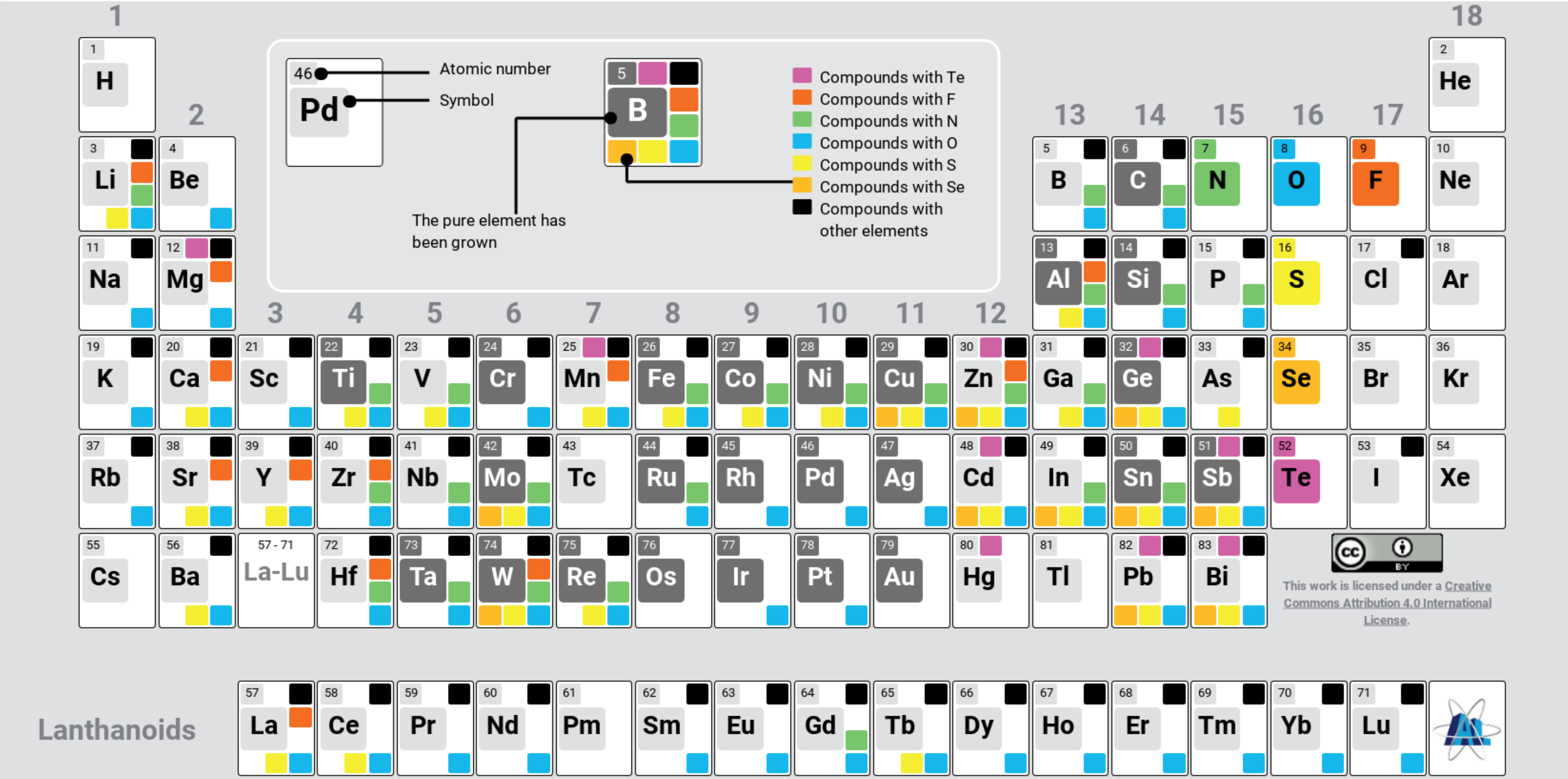






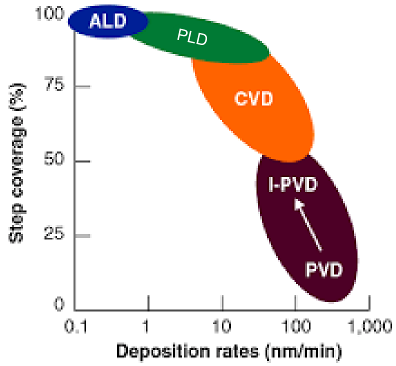


Materials Deposited by ALD



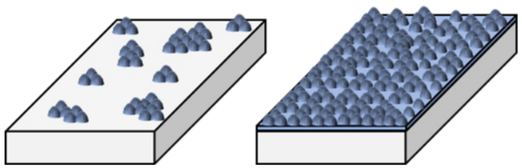
https://www.atomiclimits.com/

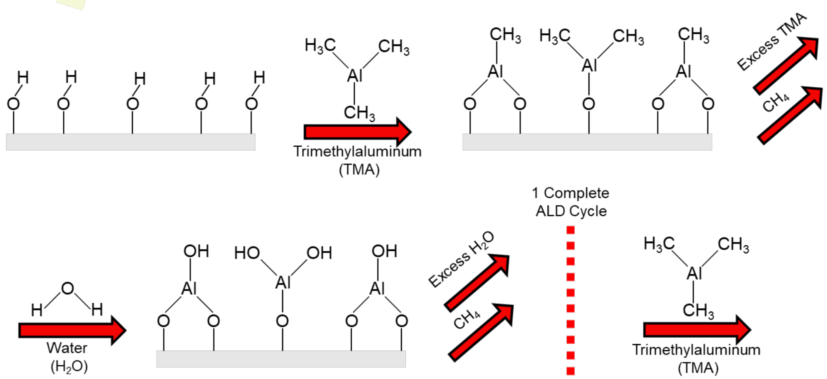
Disadvantages of ALD



- Deposition rate for ALD is much slower than other gas phase deposition technologies

- Surface functionality plays a critical role in film growth. ALD will grow around initial surface functionality – typical of metals.

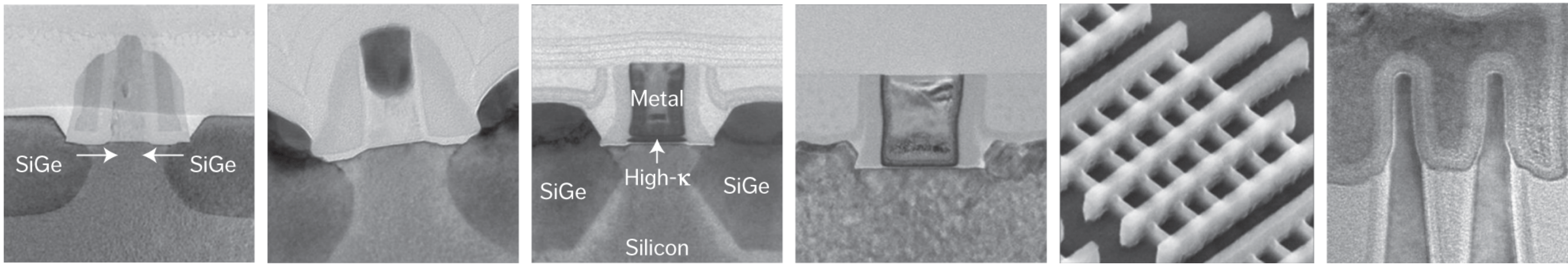


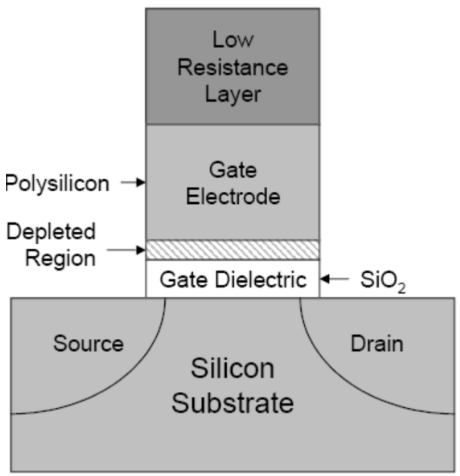


- High material waste, excess material gets pumped out.

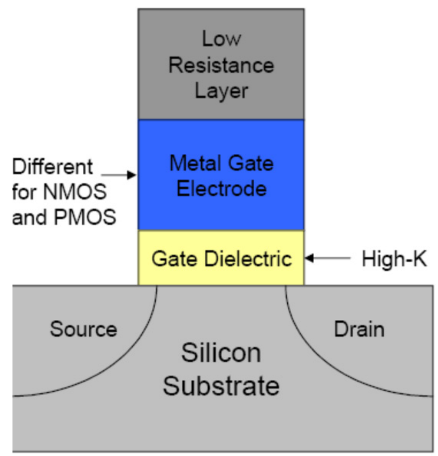
Application of ALD - Microelectronics

90 nm 2003 | 65 nm 2005 | 45 nm 2007 | 32 nm 2009 | 22 nm 2011 | 14 nm 2014

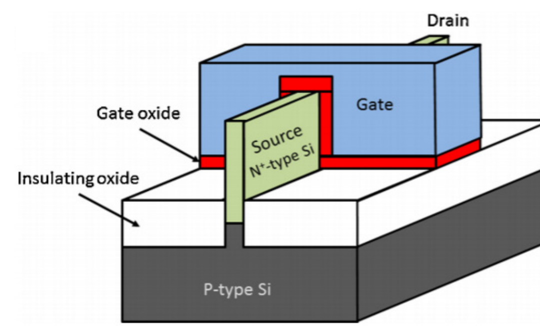




Shrinking transistor size brought gate oxide size down to 1.2nm SiO2. Unfortunately, changes would tunnel through gate and cause leaking



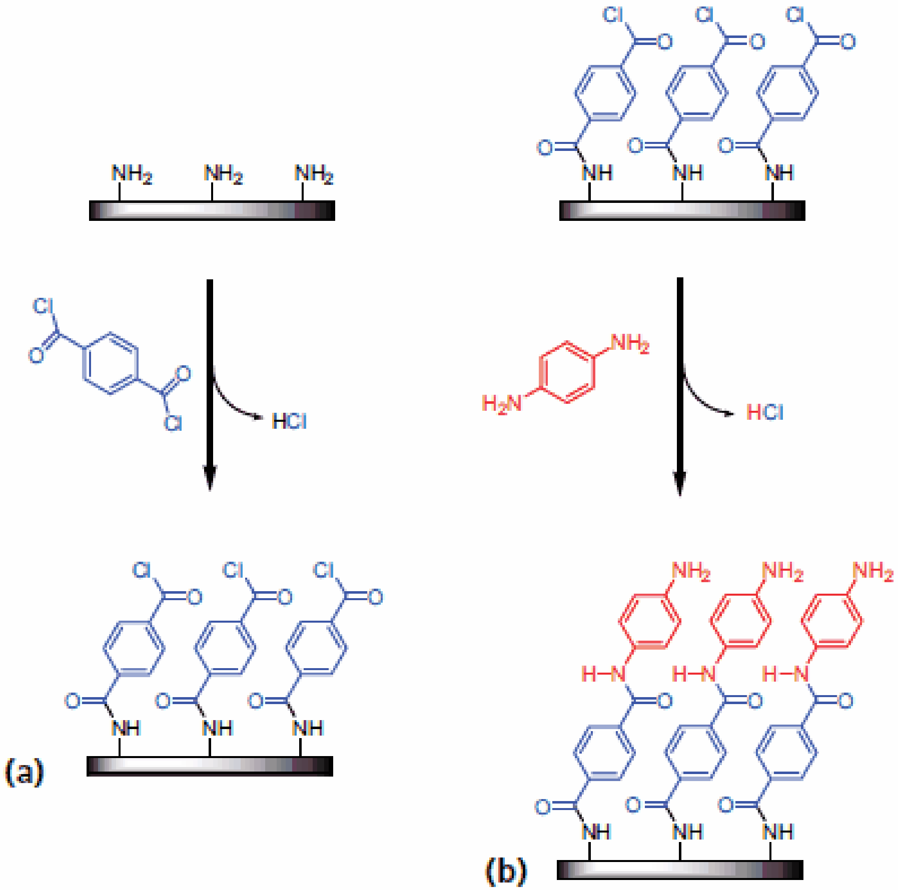
Moving to high k HfO2 gate using ALD ensure uniform gate thickness. Since field effect is increased, gate oxide can be made thicker. 100x reduction in gate dielectric leakage = lower power

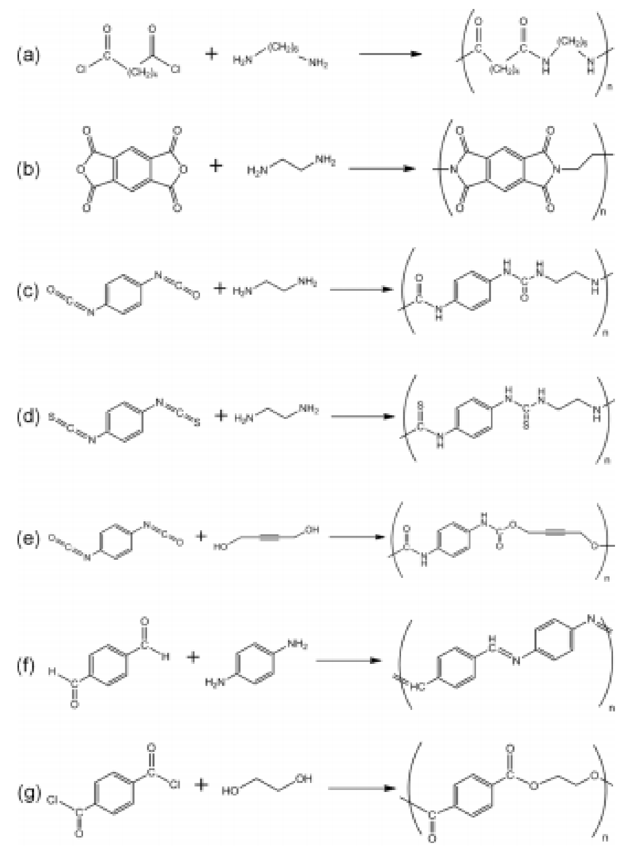


With introduction of tri-gate transistor, ALD is a key process in coating high aspect ratio fins protruding from surface with a gate oxide that is pinhole free

Extension of ALD: Molecular Layer Deposition

- In MLD molecular **bifunctional** monomer units are reacted together to form **polymeric organic materials**.

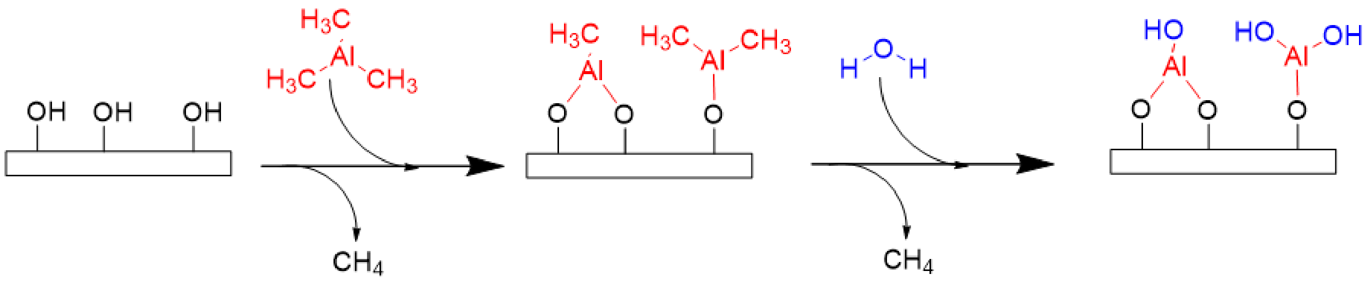




ALD vs MLD

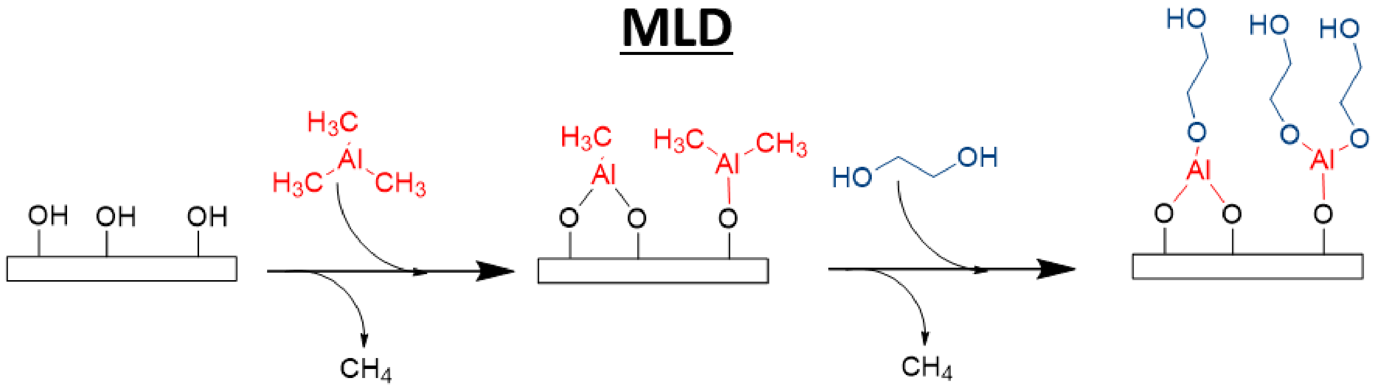
- ALD : Alternating sequences of vapour precursors allow for layer by layer growth

ALD



- ALD and MLD can be mixed together to form new metalcone compounds

MLD

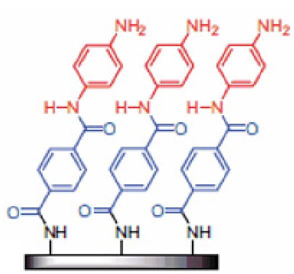


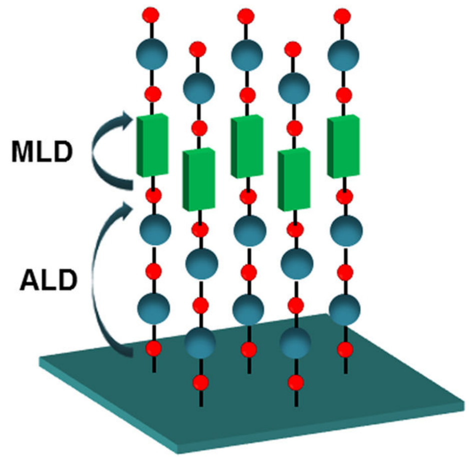
Merging ALD and MLD

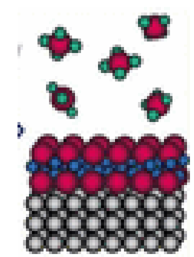
Organic (MLD) | **Inorganic (ALD)**

Organic (MLD)		Inorganic (ALD)
Soft		Hard
Flexible		Brittle
Low Modulus		High Modulus
Low Refractive Index		High Refractive Index
Low Density		High Density

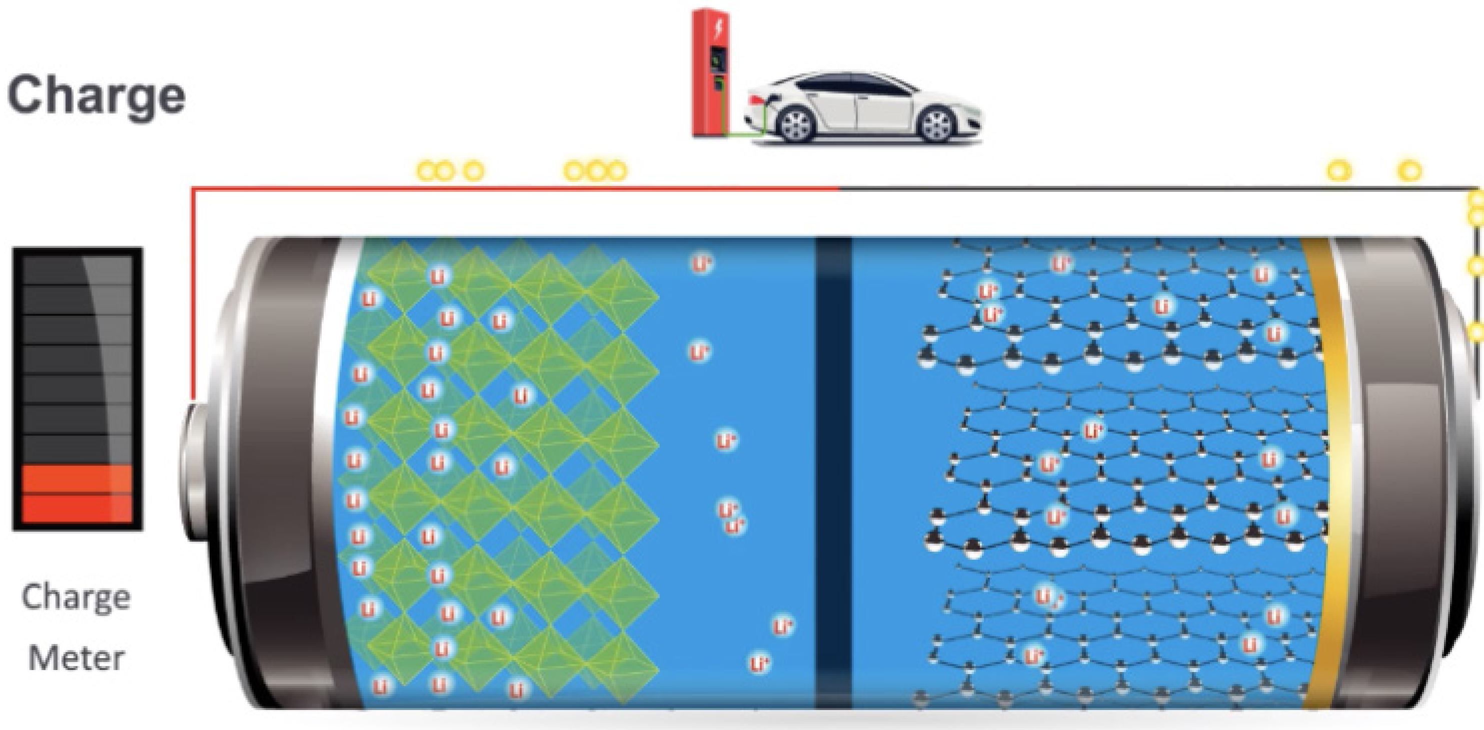
Hybrid Organic-Inorganic Films with Composite Properties



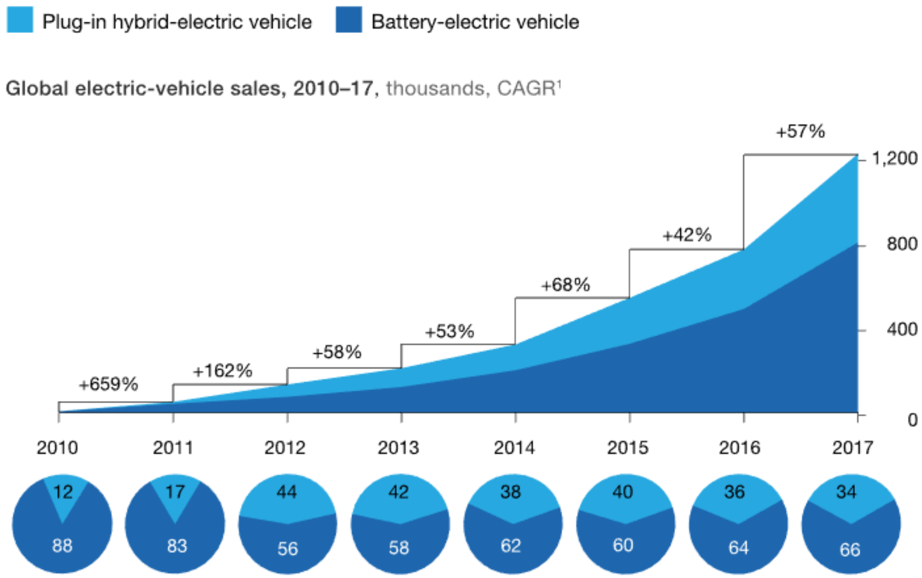




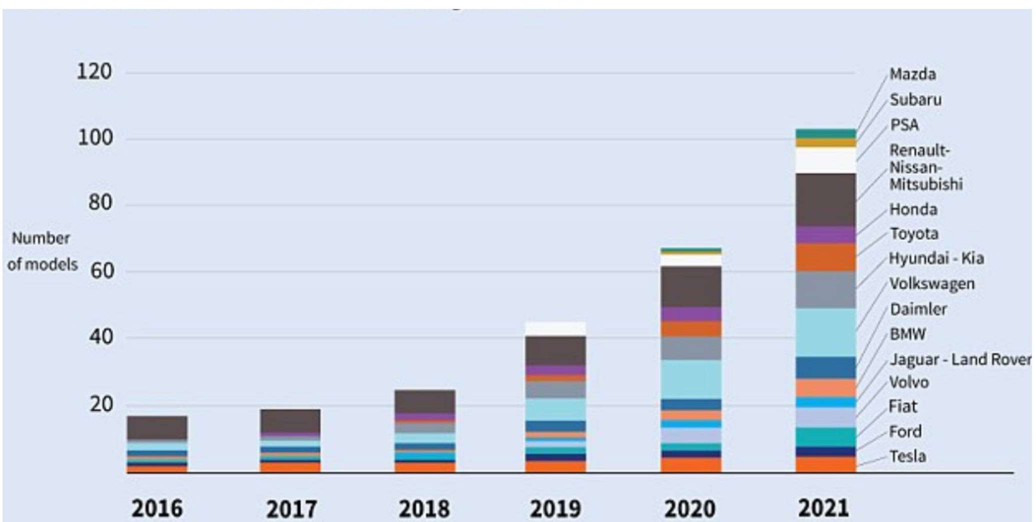
ALD and Energy Storage



Growing Electric Vehicle Market

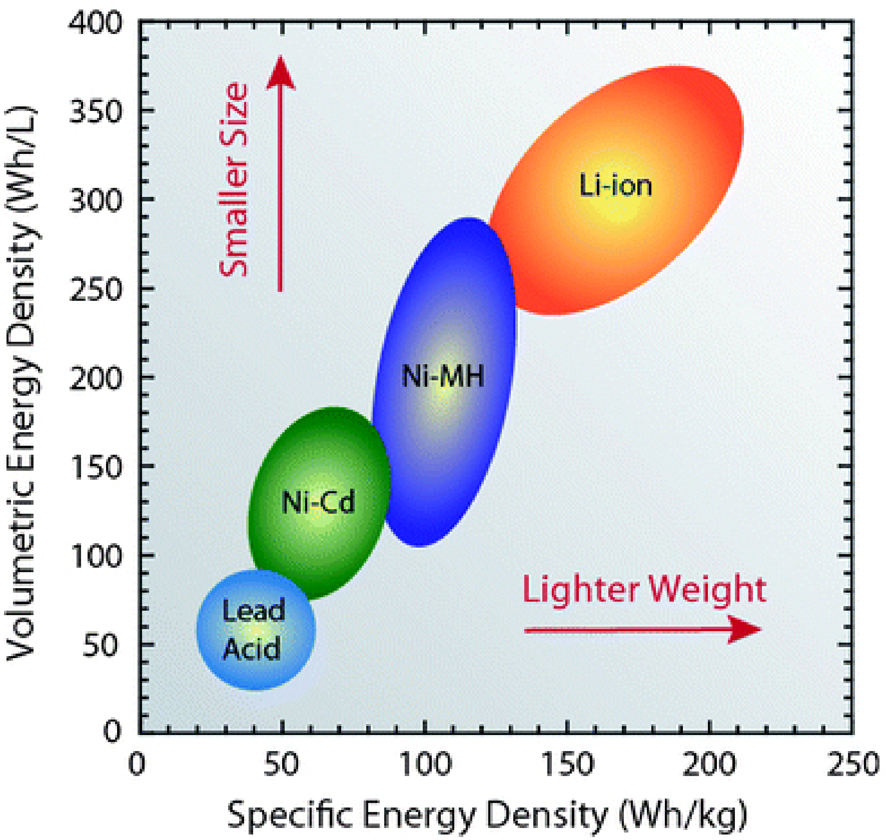


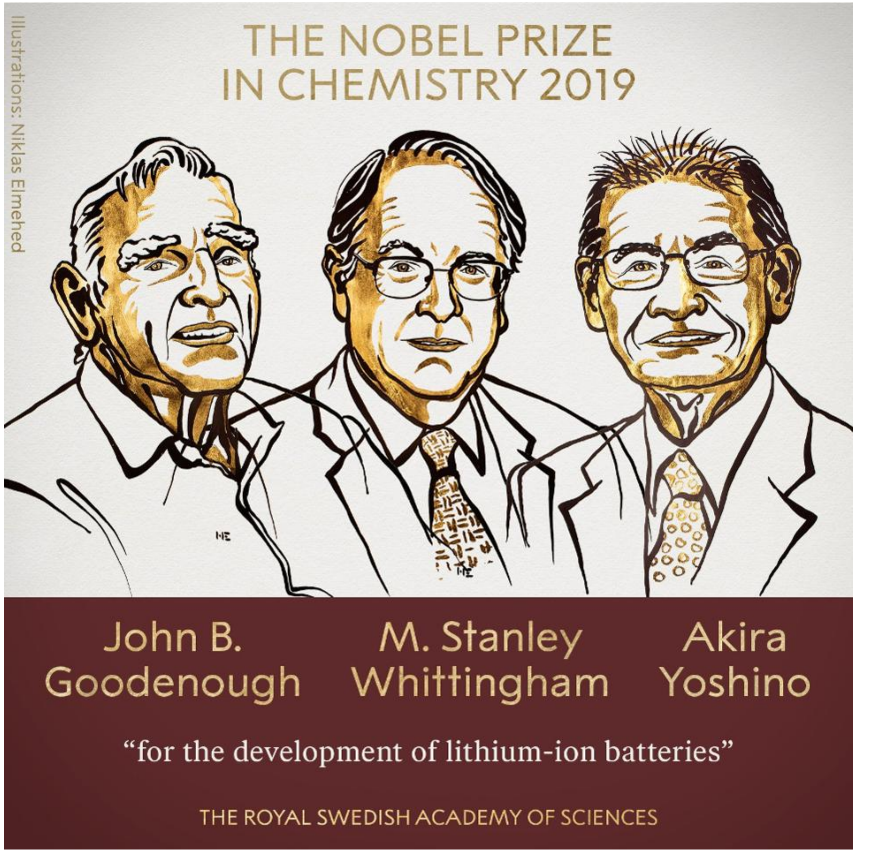
Electric vehicle market has significantly grown in the past decade



An increasing number of manufactures are entering the electric vehicle market

Energy Storage Device of Choice

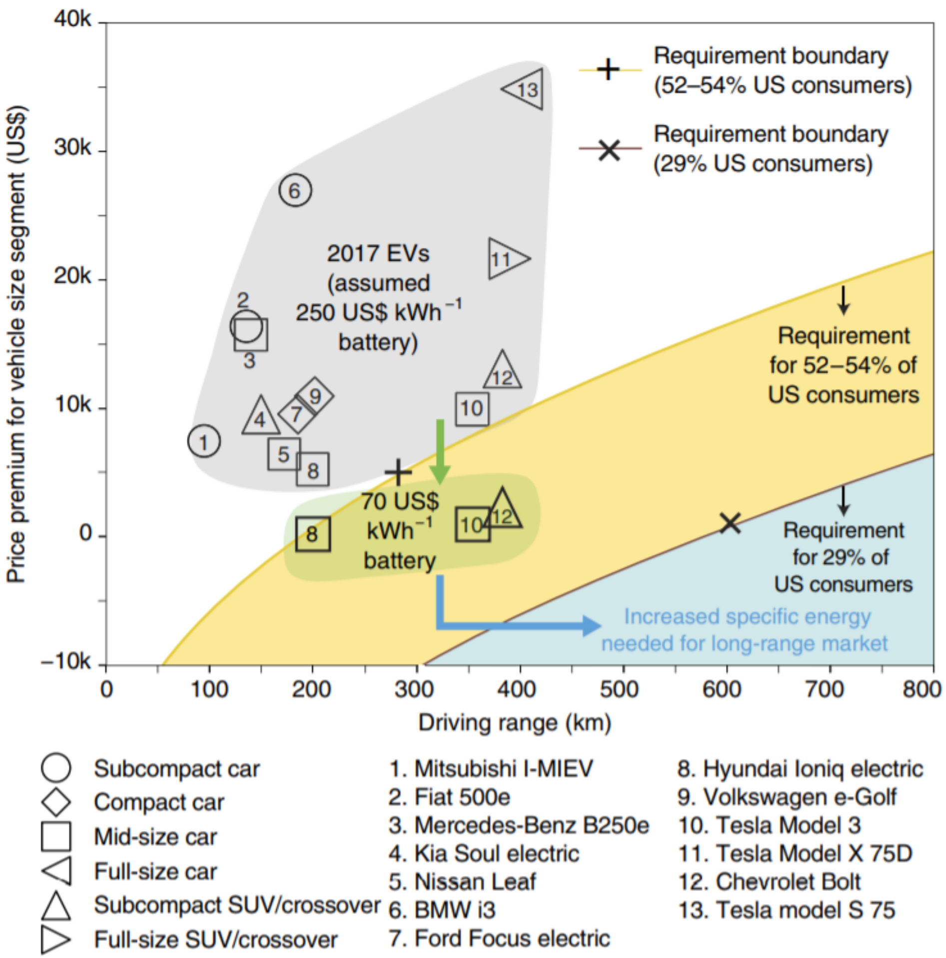


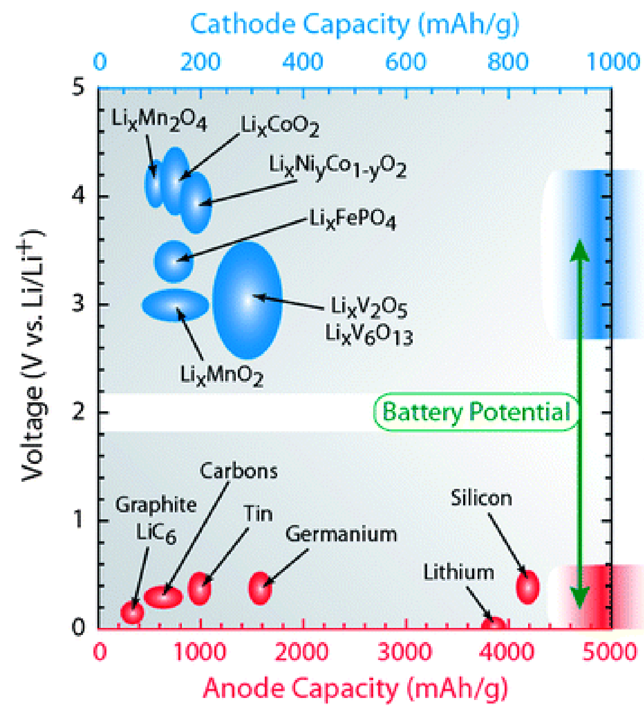


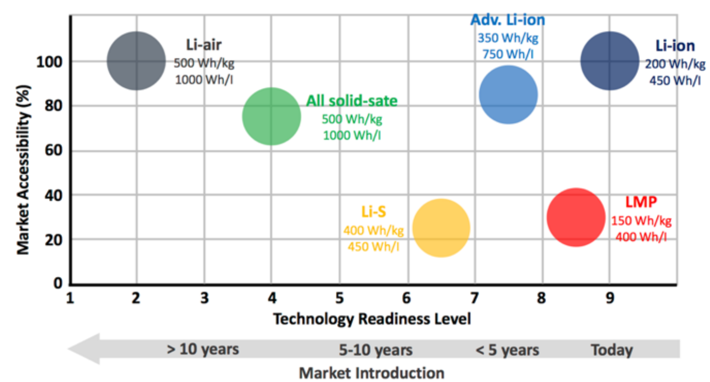
- Lithium is the lightest metal
- Lithium has a very high electrochemical potential
- Provides the largest energy density for weight out of any other battery system

New Materials Required for Future Energy Storage Devices

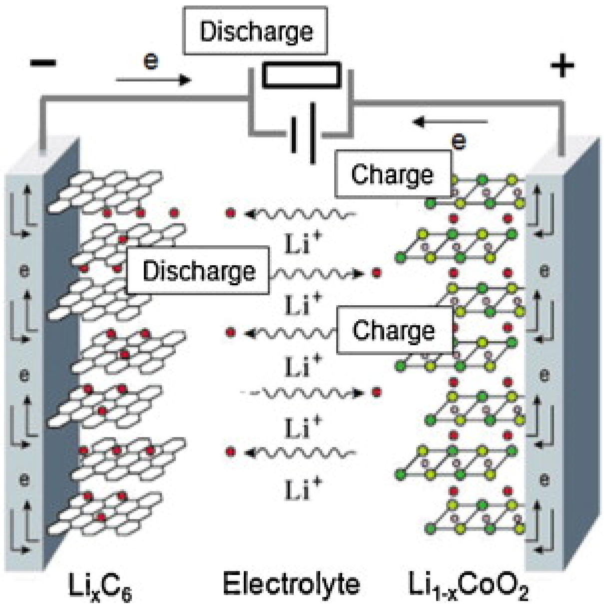
To meet future demand and extend EV range, adoption of new materials is required.

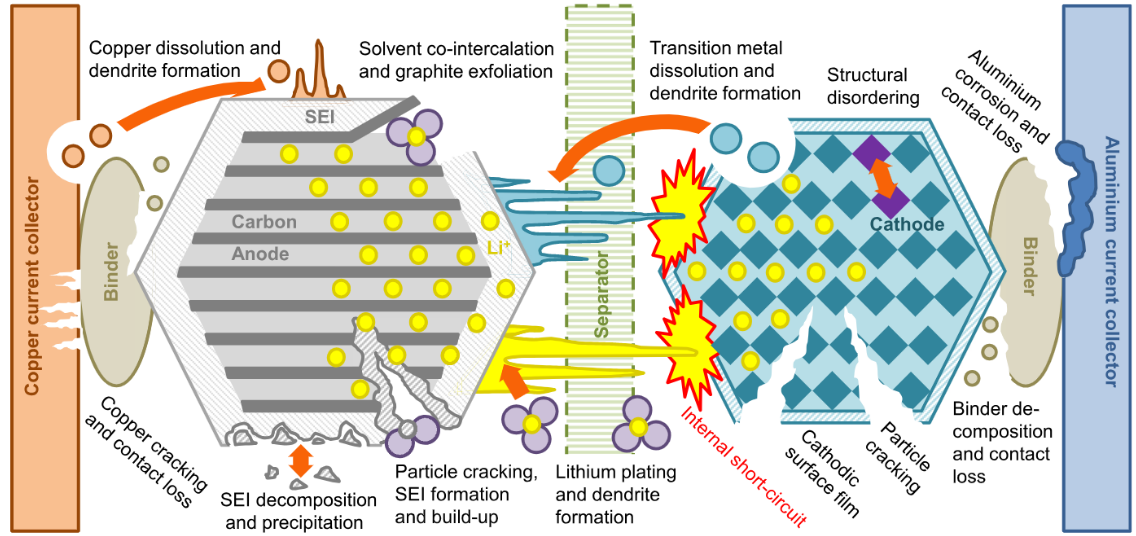


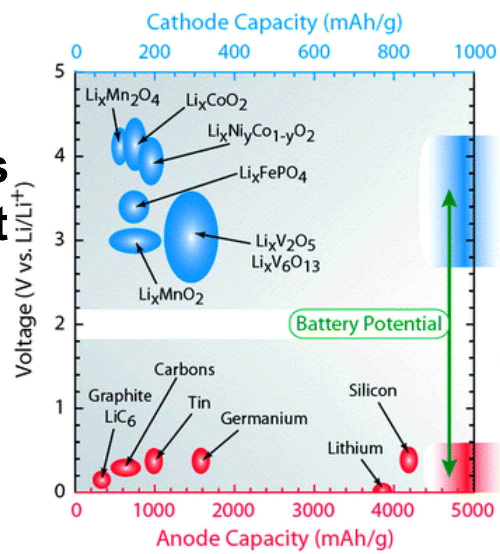




Lithium Ion Battery Operation and Challenges at the Interface

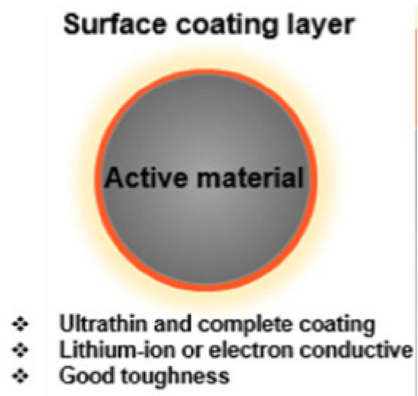


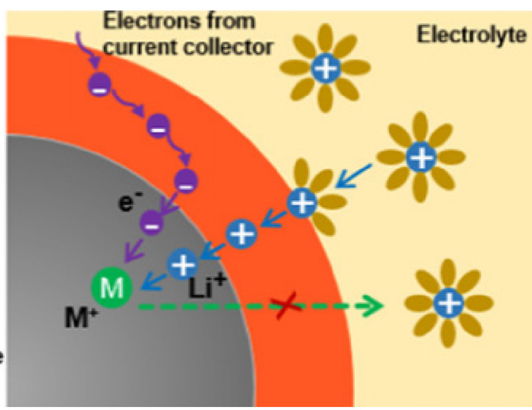


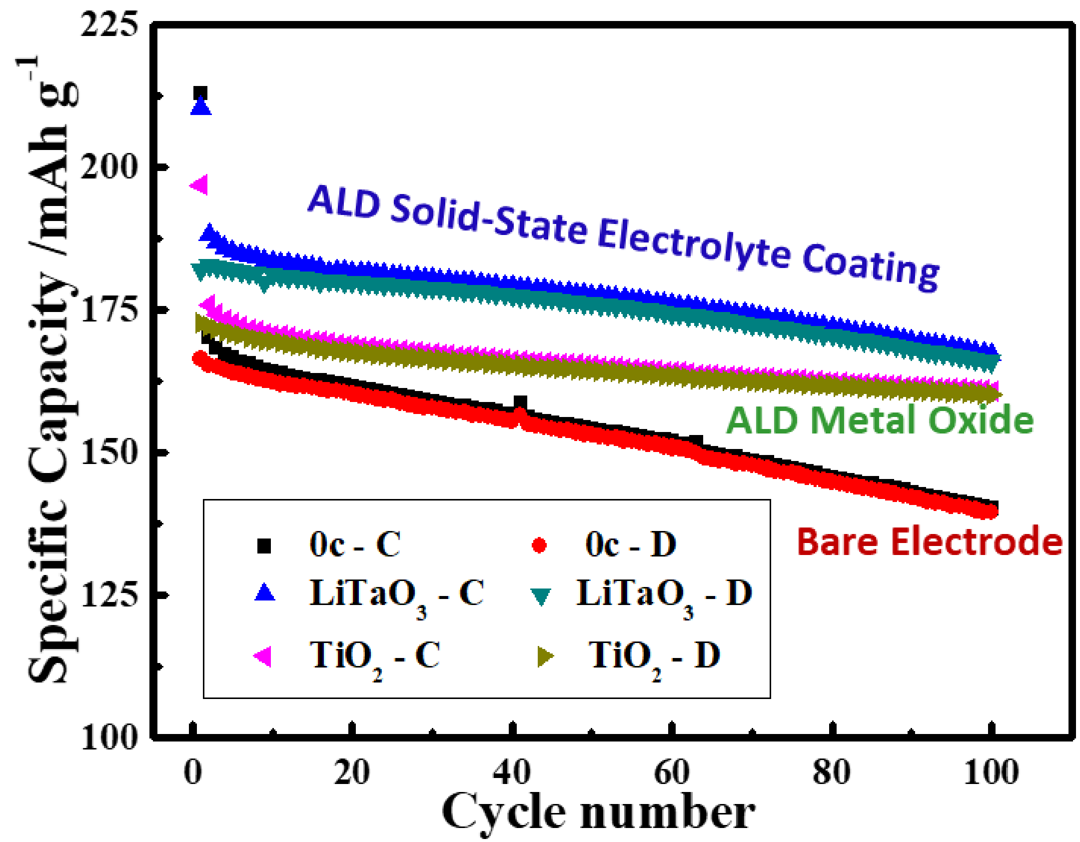


Required Coating Properties	Anode	Cathode
Uniform Coverage	☑	☑
Lithium-ion Conductive	☑	
Electronically Conductive		☑
Chemical stability	☑	☑
Prevent Metal Dissolution	☑	☑
Enhance Mechanical Stability	☑	☑

ALD Coating Enhancing Cathode Performance

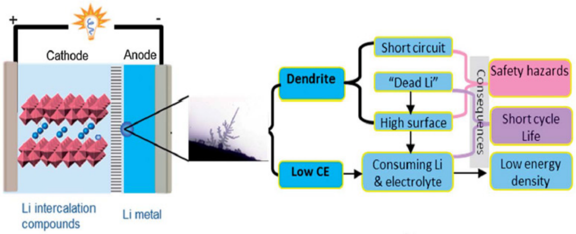


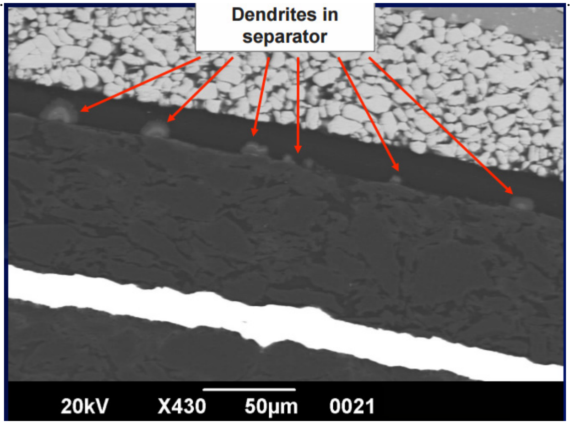


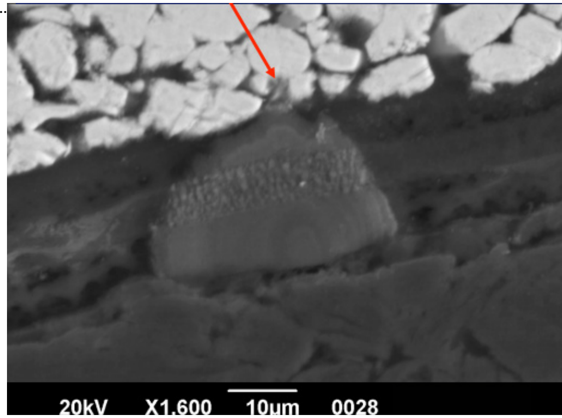


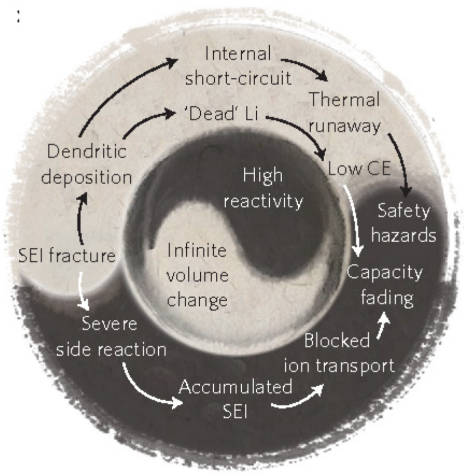
- ALD provides unique surface coverage required to mitigate metal dissolution
- ALD nanolaminates used to tune film properties, such as lithium ion diffusion.

ALD Enhancing Anode

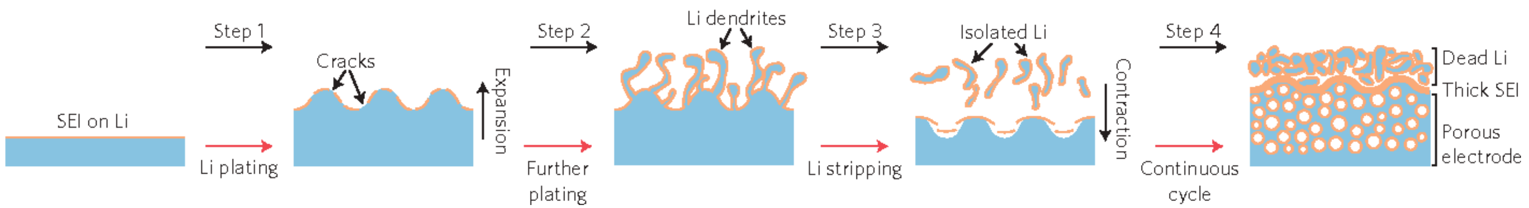






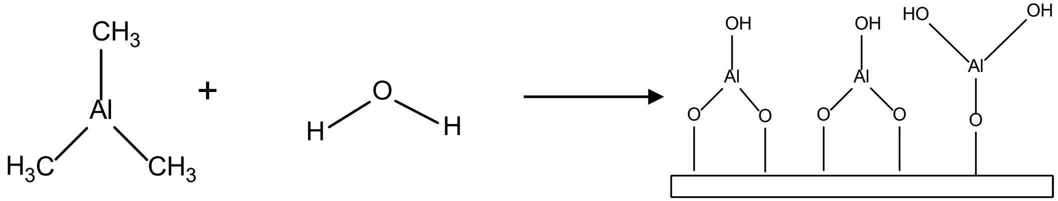


1. High Reactivity of Lithium
2. Uncontrolled Formation of Solid Electrolyte Interface (SEI)
3. Infinite Volume Change



Use of ALD and MLD to Engineer Surface

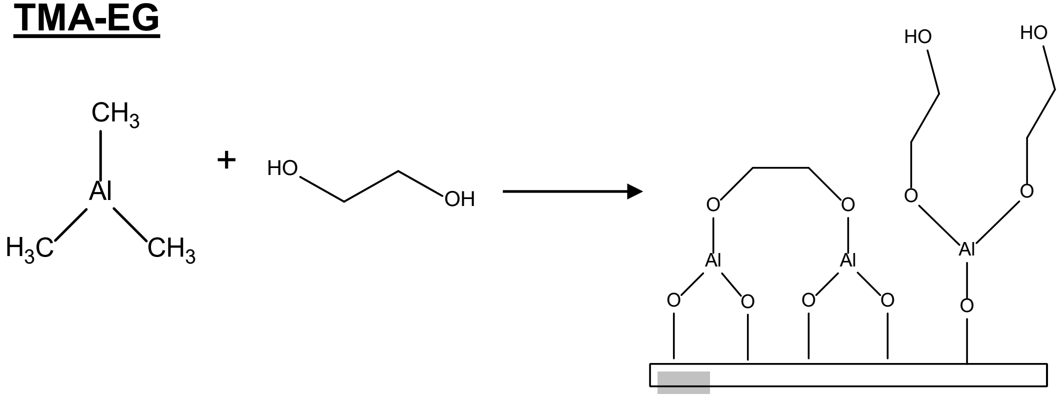
TMA-H_2O



- Previous research indicates positive results
- Can be done at low temperatures (RT)

- Water can react with Li
- Dense film may not allow for good Li^+ conduction

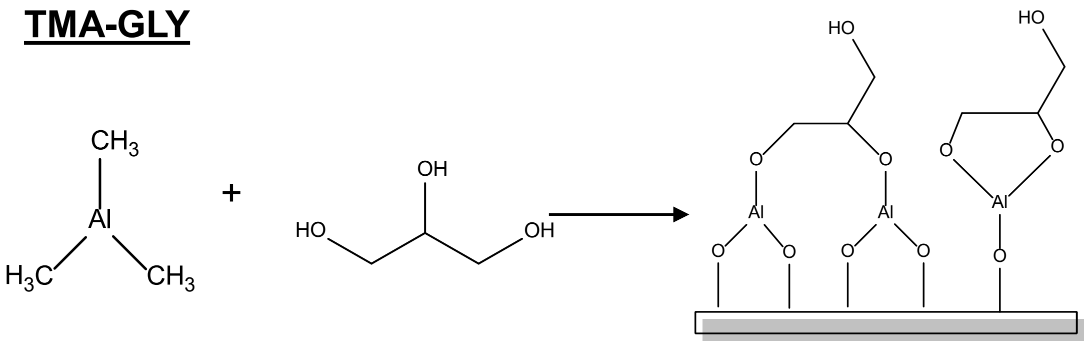
TMA-EG



- Increase film flexibility by MLD linkage
- Relatively low deposition temperature (90°C)
- Does not include water

- Increase chance of double side reactions
- Long purge times

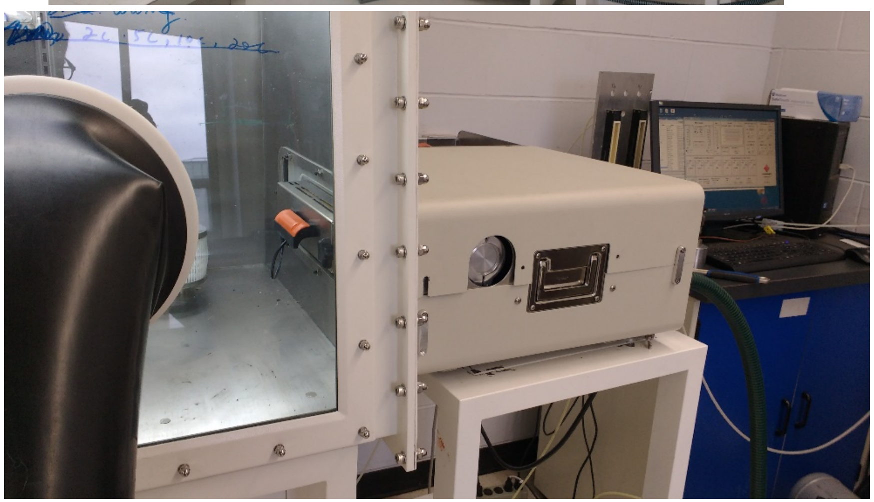
TMA-GLY

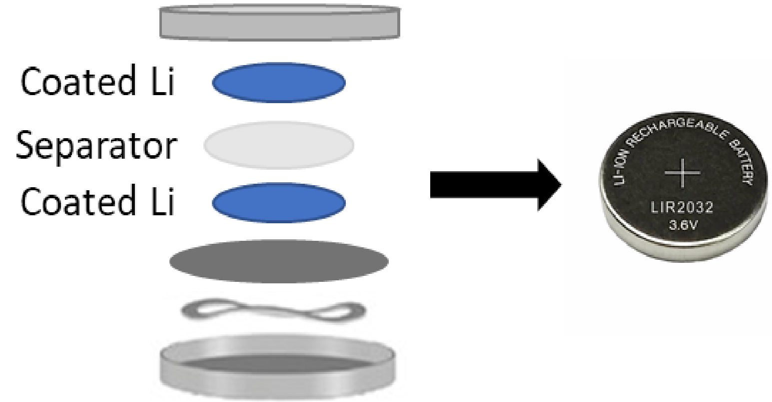


- Highly Robust
- Continued reaction (dbl side reactions do not limit surface sites)
- Increased cross linking

- Requires high deposition temperatures (150°C)
- Long purge times

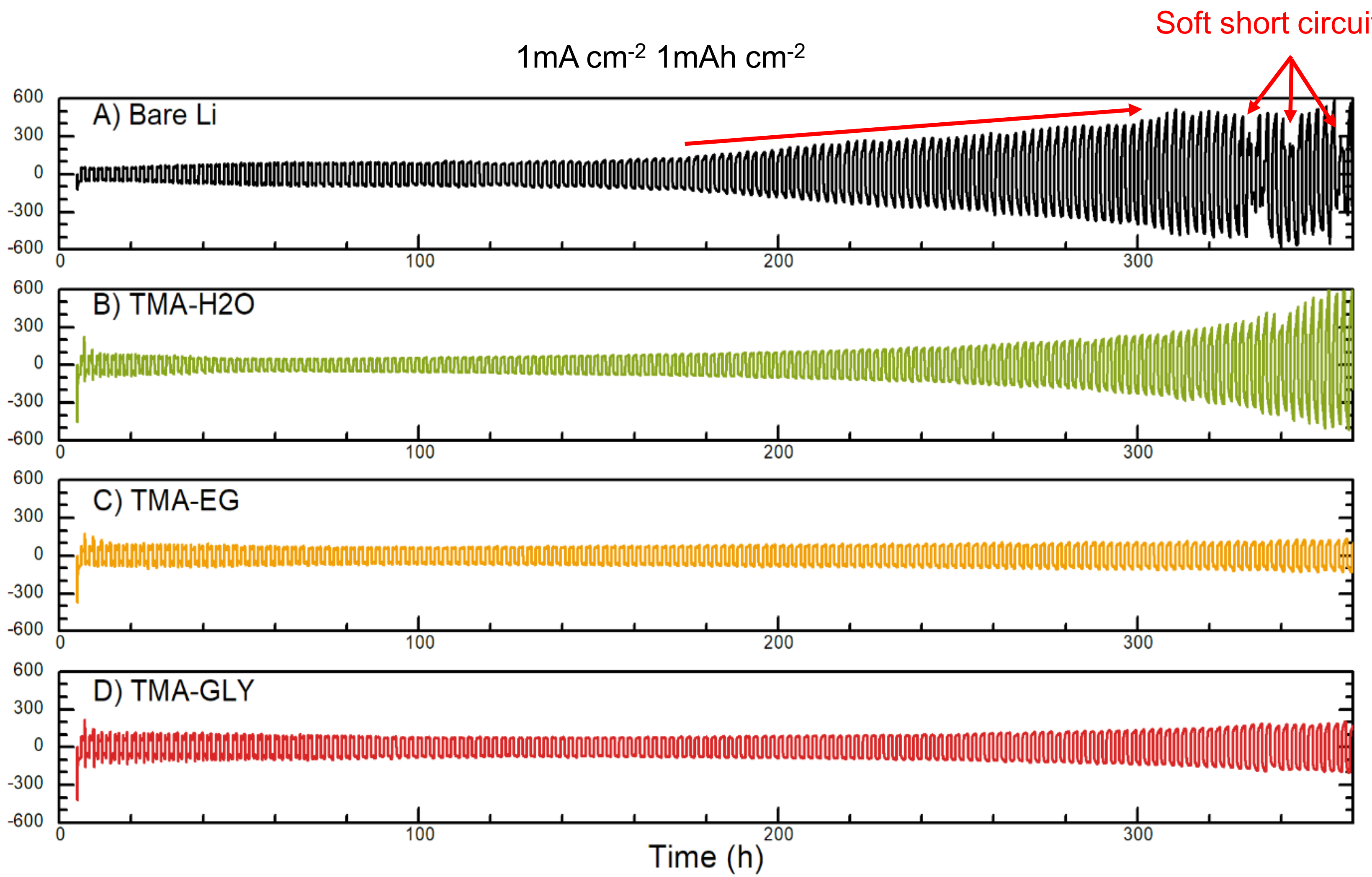
Coating Lithium with ALD/MLD





Current Density (mA cm^{-2}): How quickly Li is transferred from electrode → electrode
Capacity (mAh cm^{-2}): How much Li is transferred per charge/discharge cycle

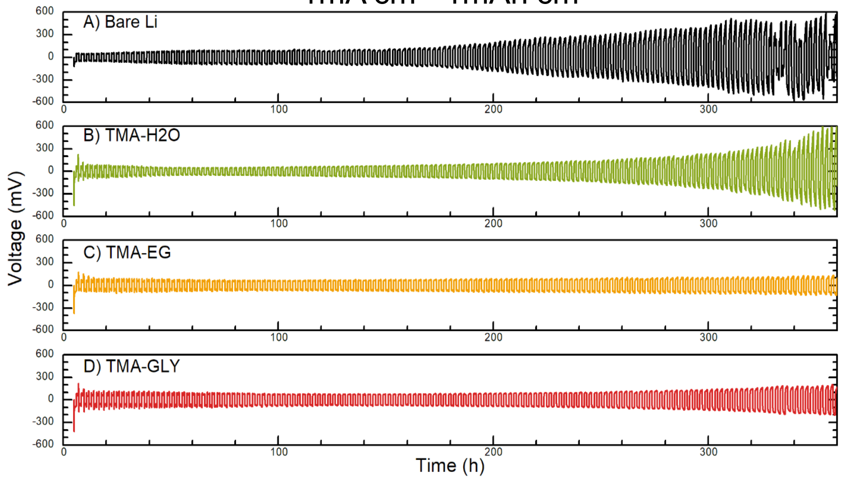
Cell Testing



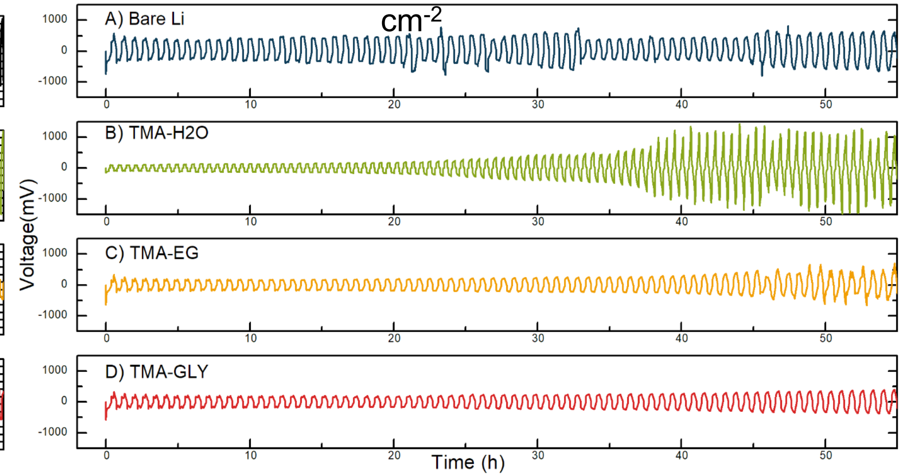
Cell Testing Continued

Current Density (mA cm^{-2}): How quickly Li is transferred from electrode → electrode
Capacity (mAh cm^{-2}): How much Li is transferred per charge/discharge cycle

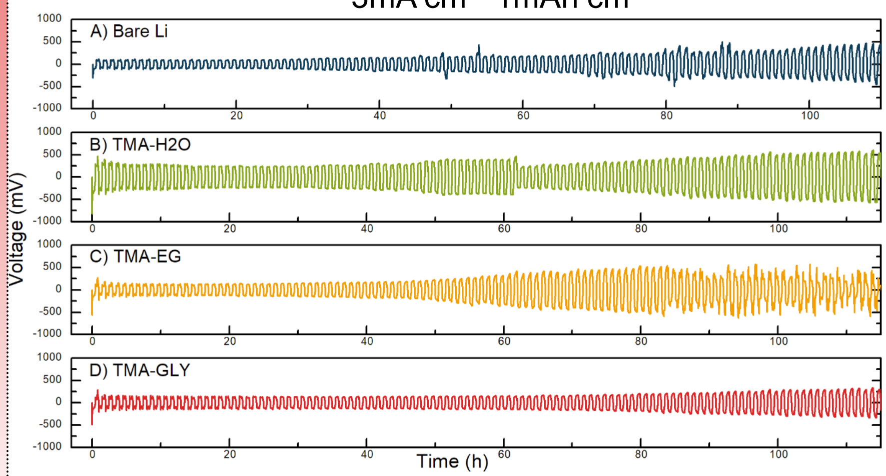
1mA cm^{-2} 1mAh cm^{-2}



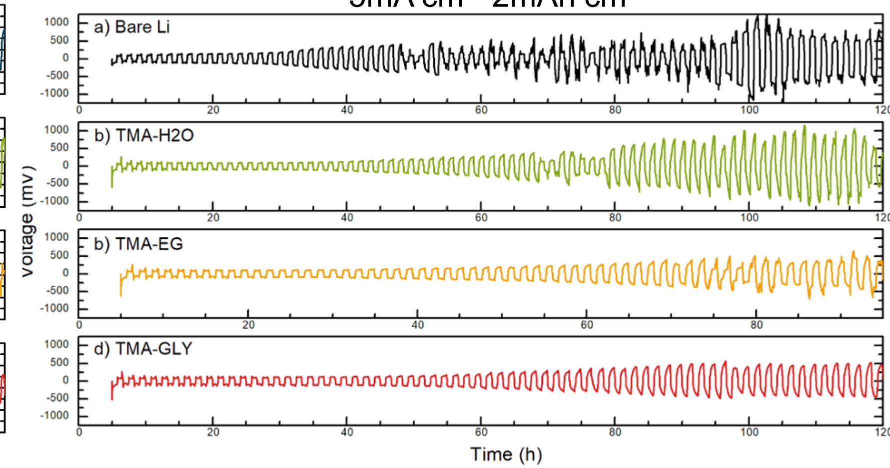
5mA cm^{-2} 1mAh cm^{-2}



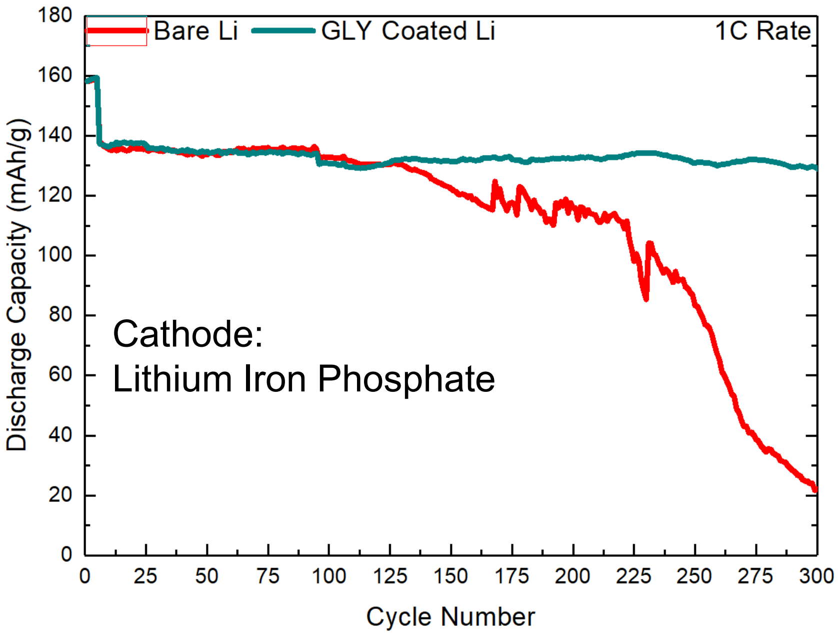
3mA cm^{-2} 1mAh cm^{-2}

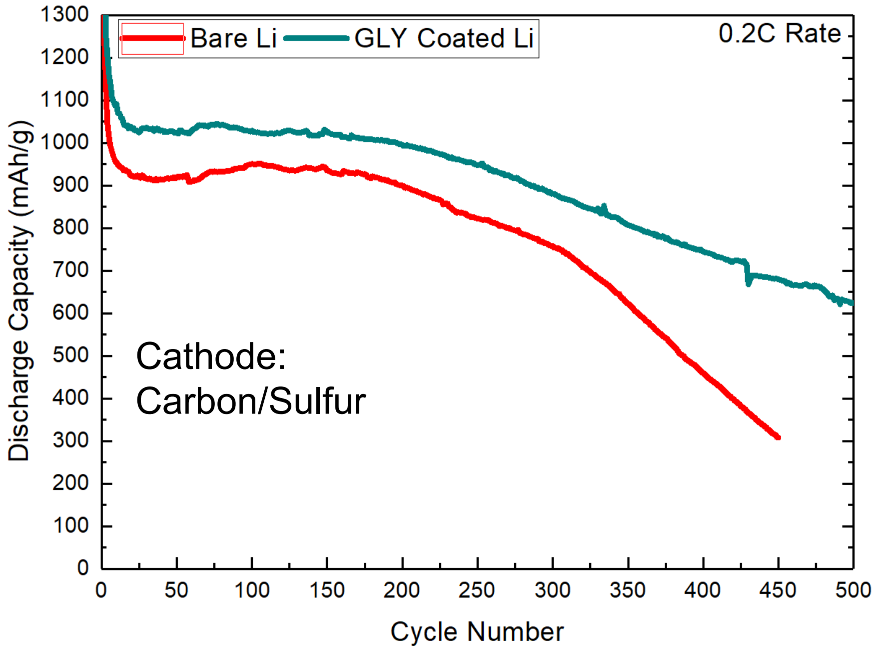


3mA cm^{-2} 2mAh cm^{-2}



Full Cell Battery Data





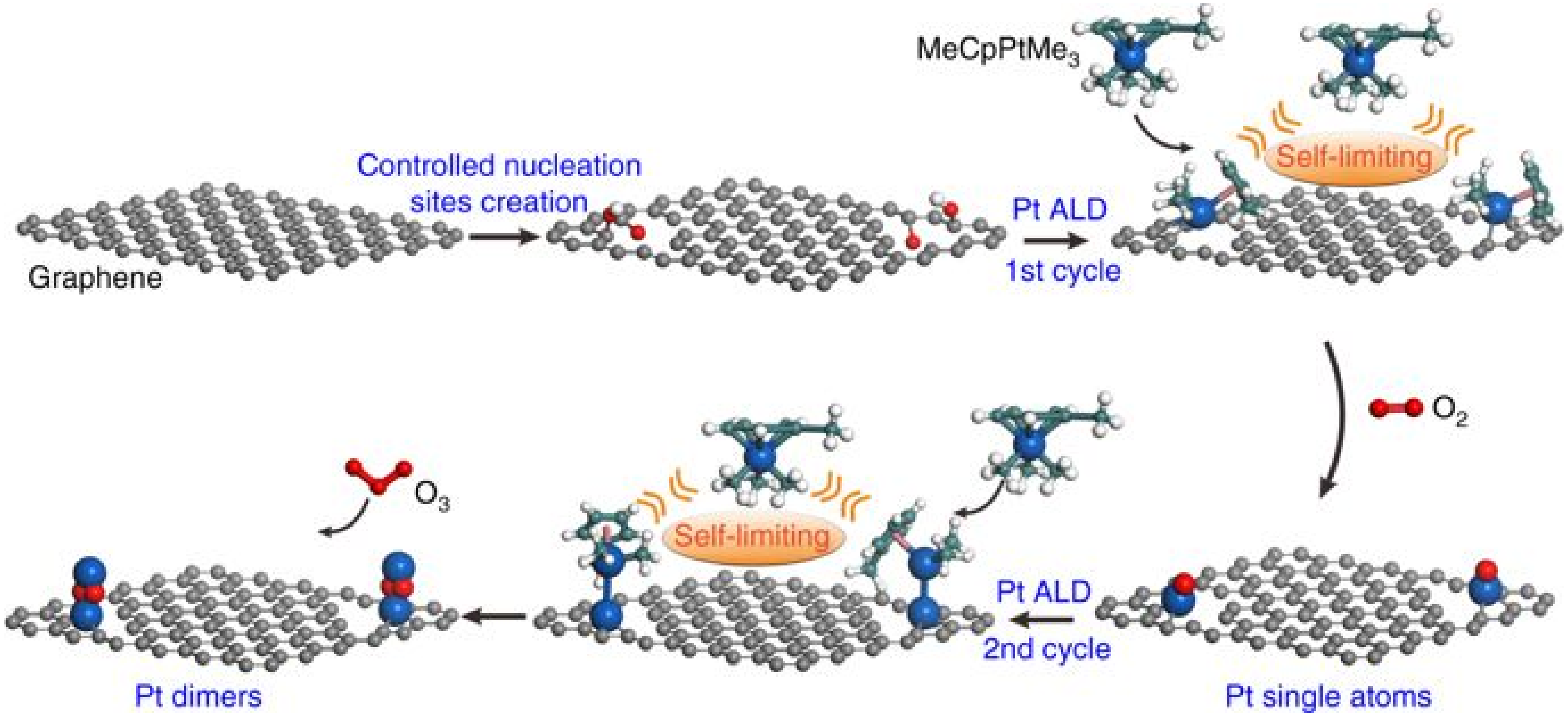
- LFP – Lithium Ion Battery
  - Considered a more environmentally friendly material compared to $LiCoO_2$
  - Coin cells tested using loading of ~ 10mg
  - Carbonate based electrolyte (1M $LiPF_6$ in EC, DEC, EMC w FEC)
  - Constant current in a voltage range of 2.5-4.2V

- Carbon/Sulfur – Lithium-Sulfur Battery
  - Much higher energy density compared to Lithium ion
  - Coin cells tested using loading of ~1mg
  - Ether Based electrolyte (1M LiTFSI in DOL, DME w $LiNO_3$)
  - Constant current in a voltage range of 1.8-2.8V

ALD and Energy Storage Summary

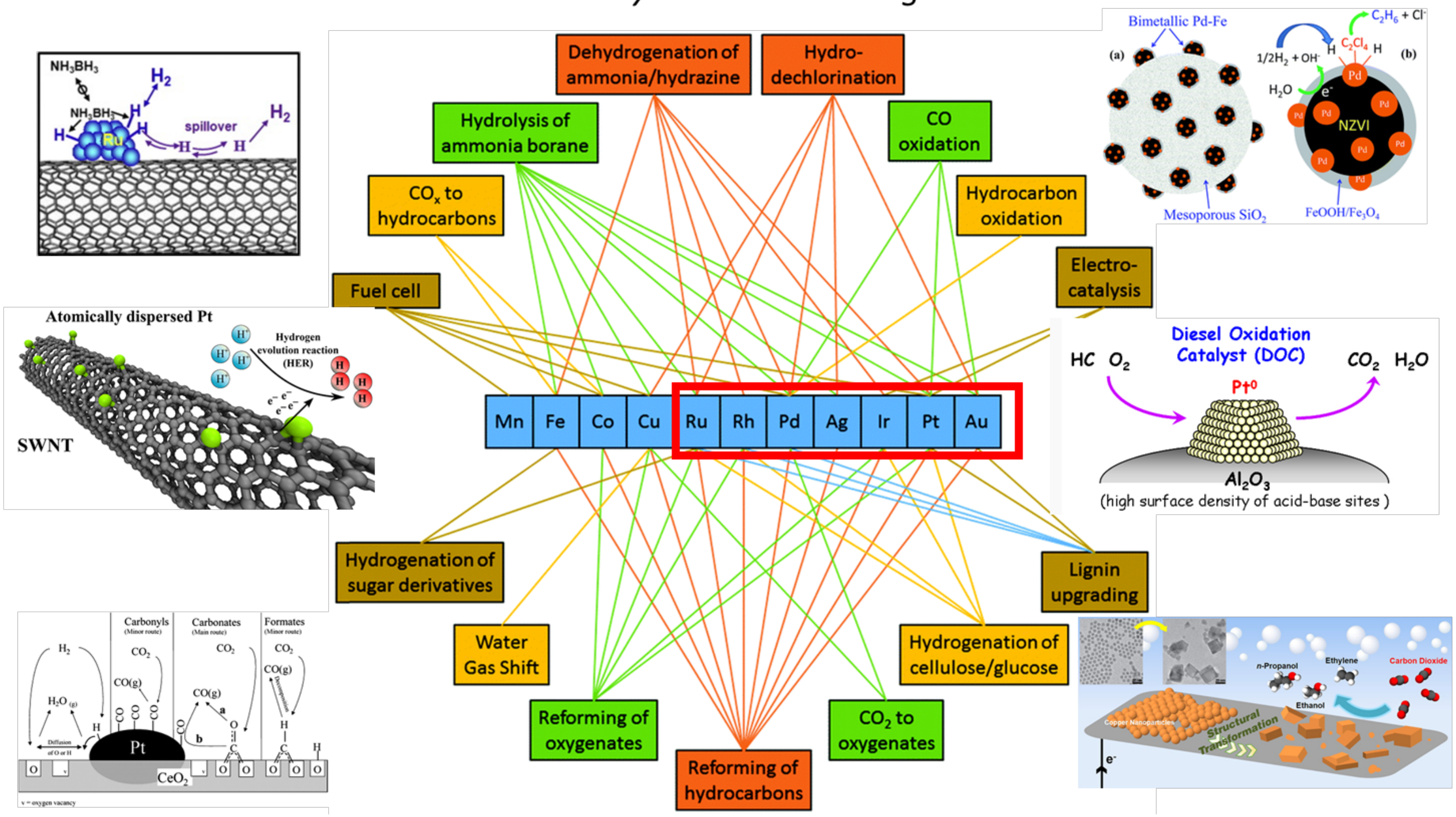
- There is a consumer demand for Energy Storage devices with increased Energy Density. However, this requires the adoption of new materials
- Many problems exist at the interface of electrode materials – ALD is one solution for addressing these problems
- For cathode materials, tuning and ALD material to be lithium ion conducting prevents metal dissolution and prolongs cycle life and capacity
- For anode materials, ALD stabilizes the interface between the electrolyte and electrode, allowing for prolonged cycling behavior.

ALD and Catalysis



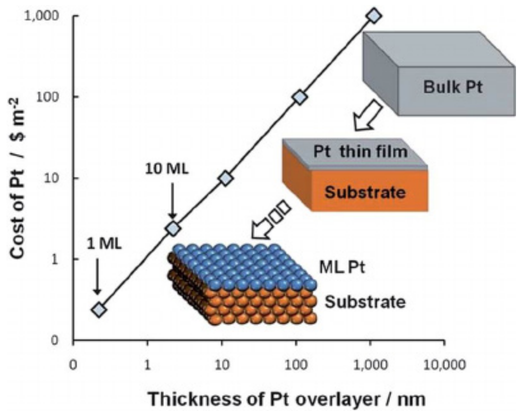
Nobel Metals Empower Catalyst Reactions

Supported noble metal catalysts nanoparticles are among the most important catalyst that enable many critical technologies

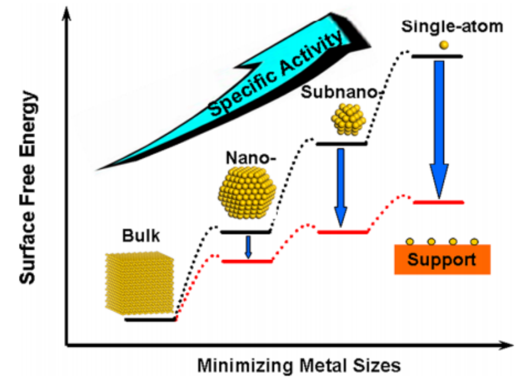


Reducing Size of Catalyst Particles

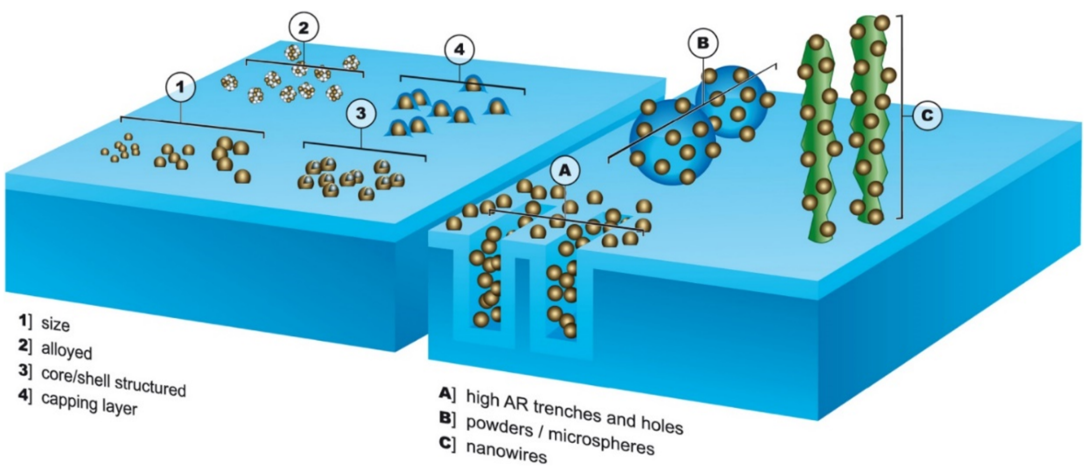
High price and low natural abundance of noble metals is an issue.



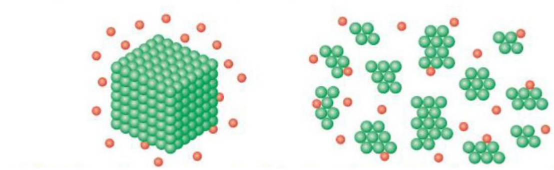
Important aspect that determines catalytic performance is nanocatalyst size



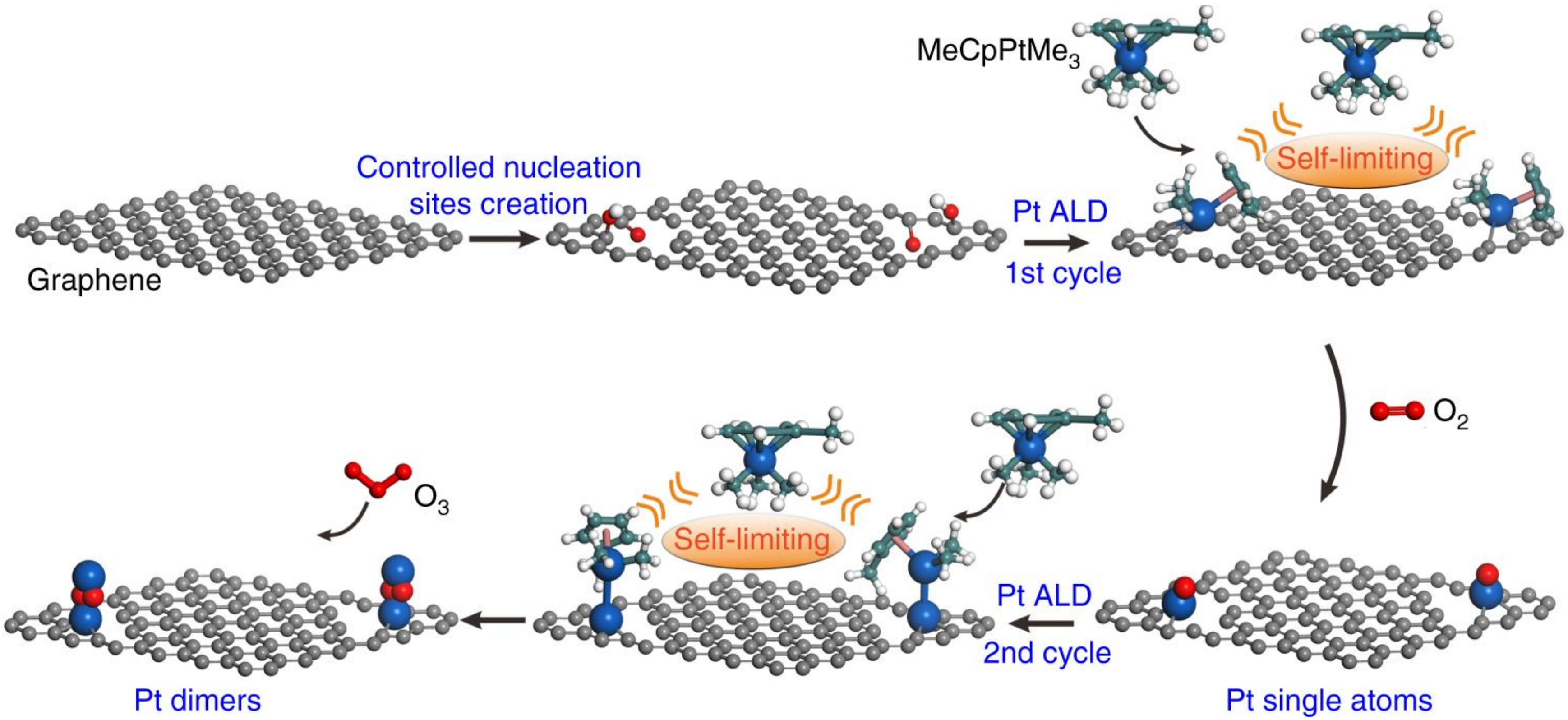
ALD has unique advantages for deposition of particles by allowing control over:



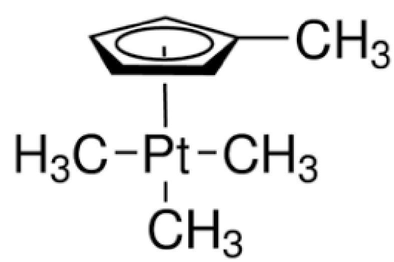
Increased surface area also increases the rate of reaction by increasing the collision frequency



Depositing Single Atoms using ALD



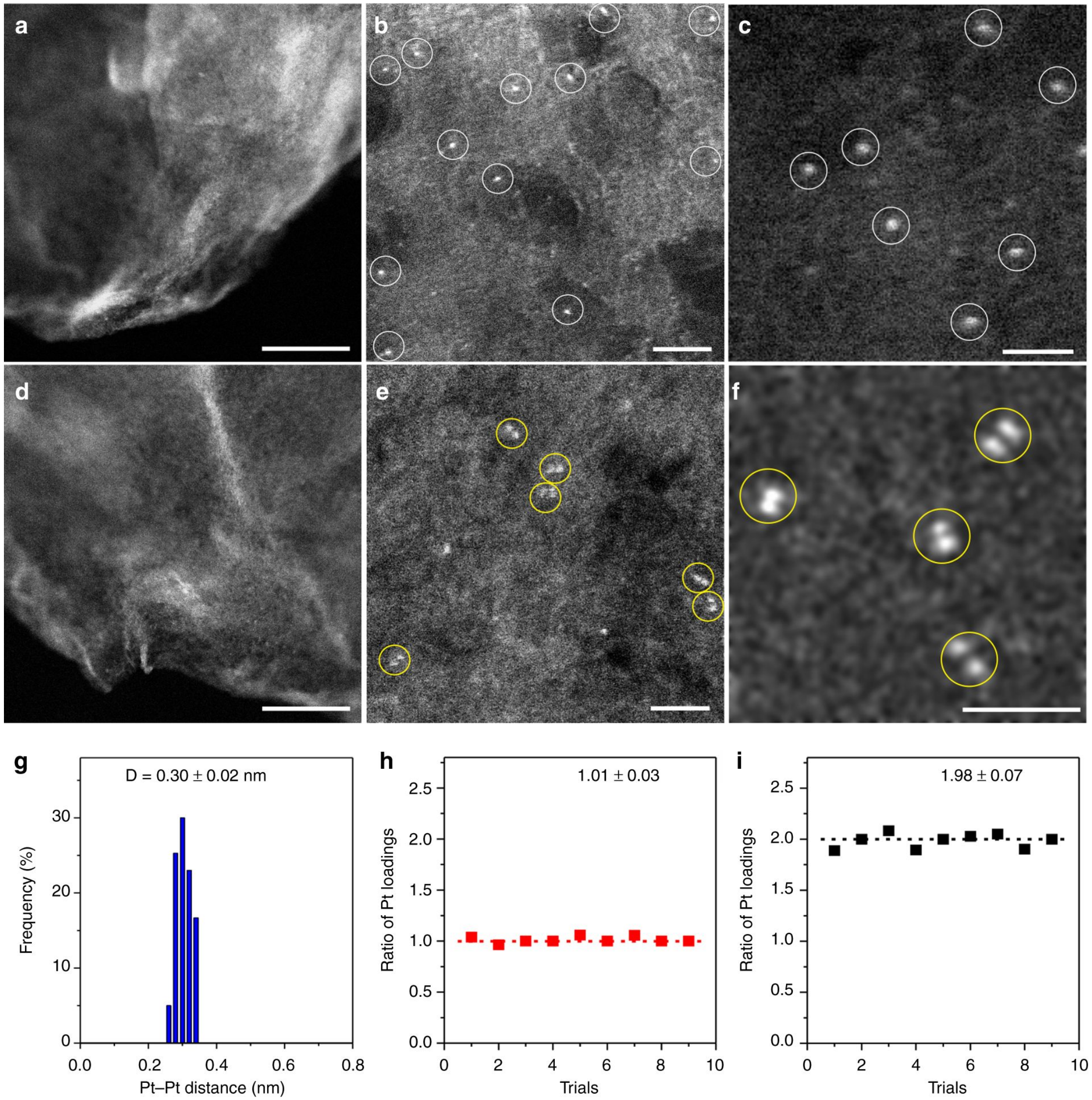
Reaction Temperature = 150C



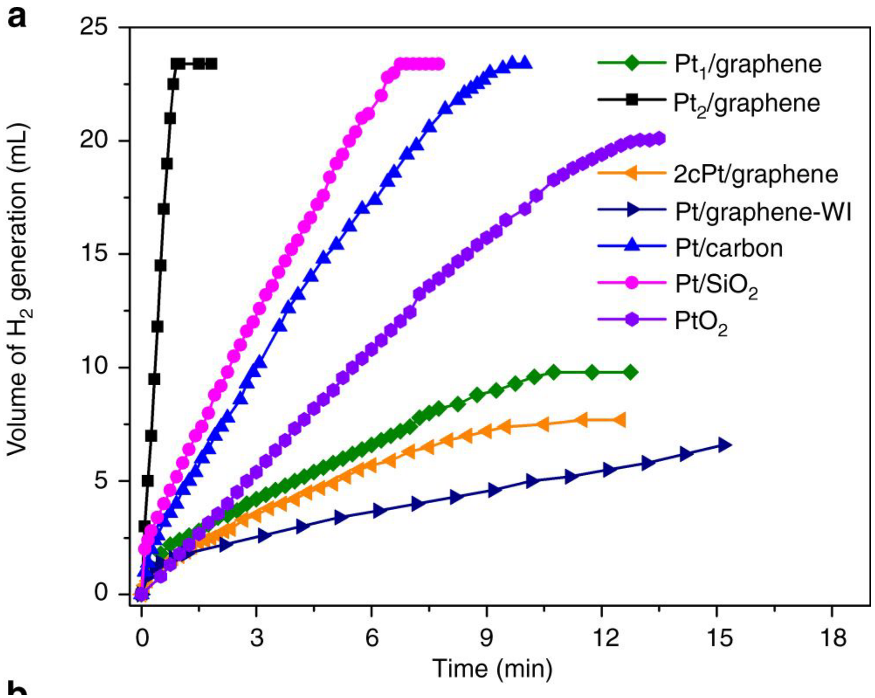
Reaction Temperature = 250C

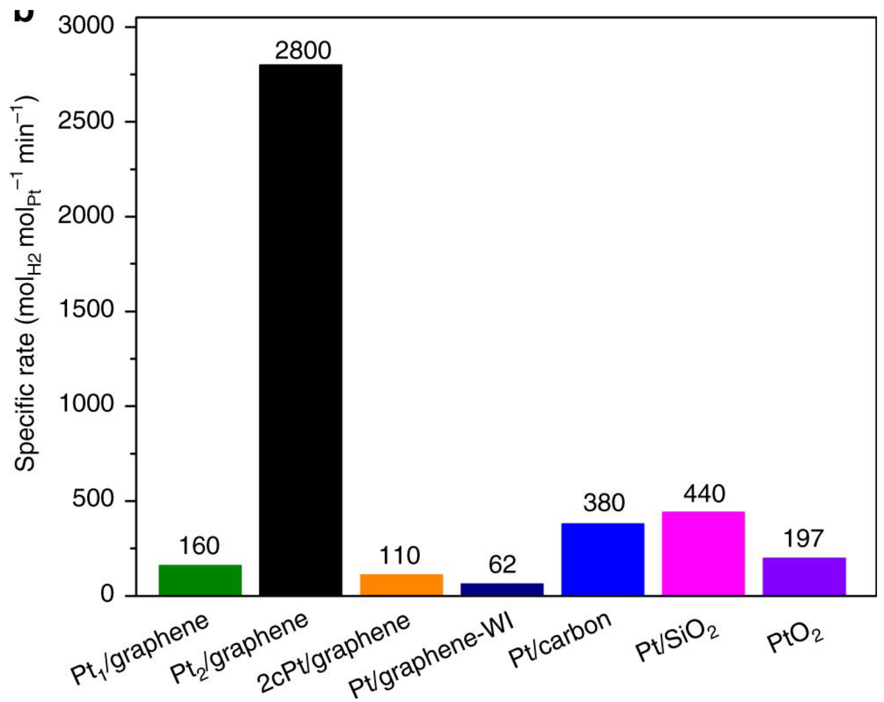
Control temperature for selective deposition

TEM Images of ALD Deposited Platinum



Hydrogen Production





Tested Pt Dimer on graphene for hydrogen production via hydrolysis of ammonia borane

17x increased hydrogen vs single atom Pt
45x vs Pt nanoparticles

$$NH_3BH_3 + 2H_2O \rightarrow NH_4^+ + BO_2^- + 3H_2\,(g)$$

ALD and Catalysis Summary

- Nobel Metals are important for a number of catalytic reactions
- Nobel metals are expensive and there is a commercial drive to reduce the utilization of these expensive materials. Furthermore, decreasing size can also increase catalytic activity
- ALD is one technique that can be used to deposit nanoparticles of noble particles down to the single atom range, providing excellent control over particle size and dimension

Conclusions and Final Remarks

- ALD is a technique that is capable of depositing angstrom level films over high aspect ratio nanostructures surfaces
- There are number of parameters that can be tuned to optimize films properties. The process is not as simple as A-B deposition.
- ALD can be used to address changes in lithium ion battery devices at both the anode and cathode
- Nanoparticles can be deposited by ALD, down to the single atom