Development of Industrially Viable Electrode Coatings

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NREL is a national laboratory of the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, operated by the Alliance for Sustainable Energy, LLC.

Overview

Timeline

- **Project start date:** 12/2011
- **Project end date: On-going**
- **Percent complete: TBD**

Barriers

- Limited calendar and cycle life
- Abuse tolerance
- High cost

Budget

- **Total project funding:**
  - DOE share: $600K
  - Contractor share: N/A
- **Funding received in FY14:** $75K
- **Funding for FY15:** $150K

Partners

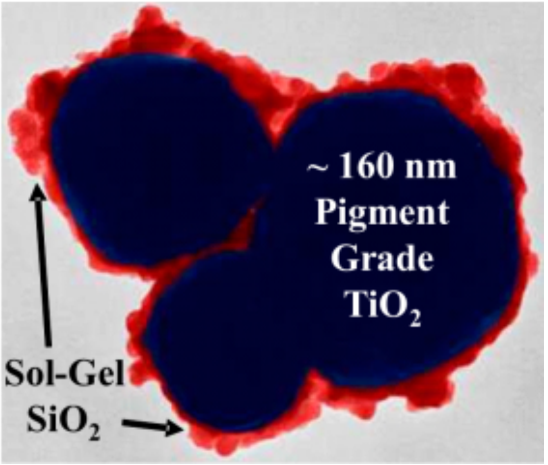
- NREL (Lead)
- University of Colorado – Boulder
- Argonne National Laboratory
- Oak Ridge National Laboratory

Relevance and Objective

- The ABR program is focused on improving cycle life, abuse tolerance and reducing cost for PHEV battery technologies.
- Previous work conducted by NREL and the University of Colorado at Boulder has demonstrated that thin, conformal coatings of lithium ion battery electrodes formed by atomic layer deposition (ALD) can dramatically improve abuse tolerance and cycle life which reduces cost.
- Current technology for performing ALD is not amenable to high throughput manufacturing methods and thus represents a high priced bottleneck in the implementation.
- ***The objective of this current work*** is the development of a system for deposition of thin protective electrode coatings using a novel "in-line" atmospheric pressure atomic layer deposition (AP-ALD) reactor design that can be integrated into manufacturing to address needs for improvement in rate capability, cycle life, and abuse tolerance in a cost effective manner.
- In addition, NREL works as part of a multi-lab collaborative team by providing ALD coating and characterization services.

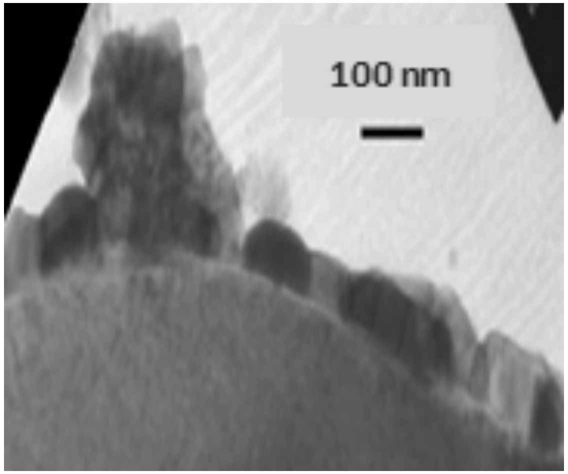
Approach - Comparison of Common Coating Technologies

Sol-Gel

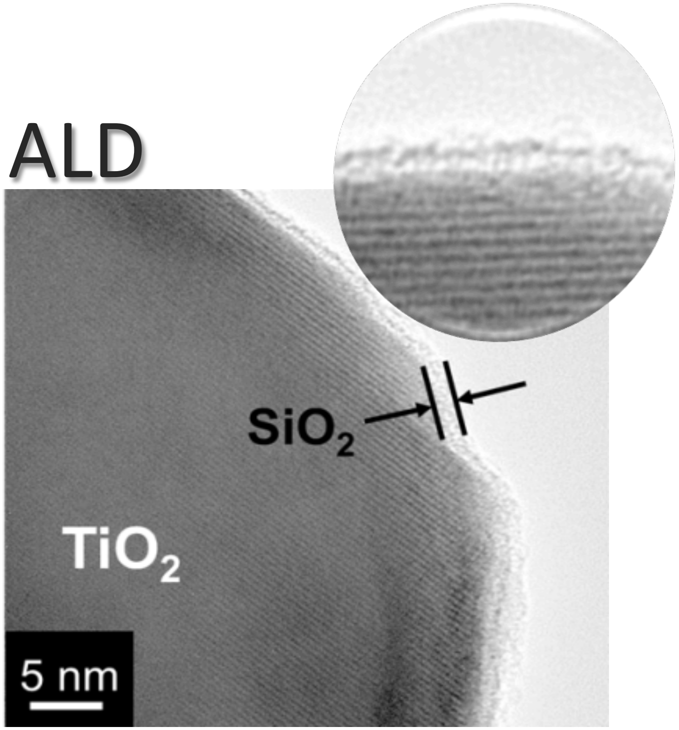


ALD uses gas phase reactions to deposit conformal coatings on porous or nanostructured materials

CVD



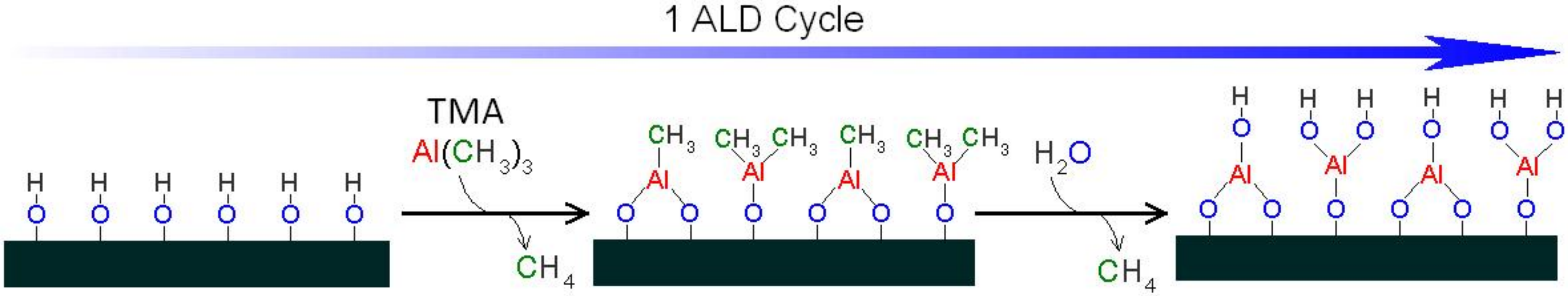
ALD



Comparable particle coating technologies cannot produce the precision or quality films of ALD

Approach: Atomic Layer Deposition (ALD) for Industrial Application: Novel Atmospheric Processing ALD (AP-ALD)

Sequential & self-limiting surface reactions:

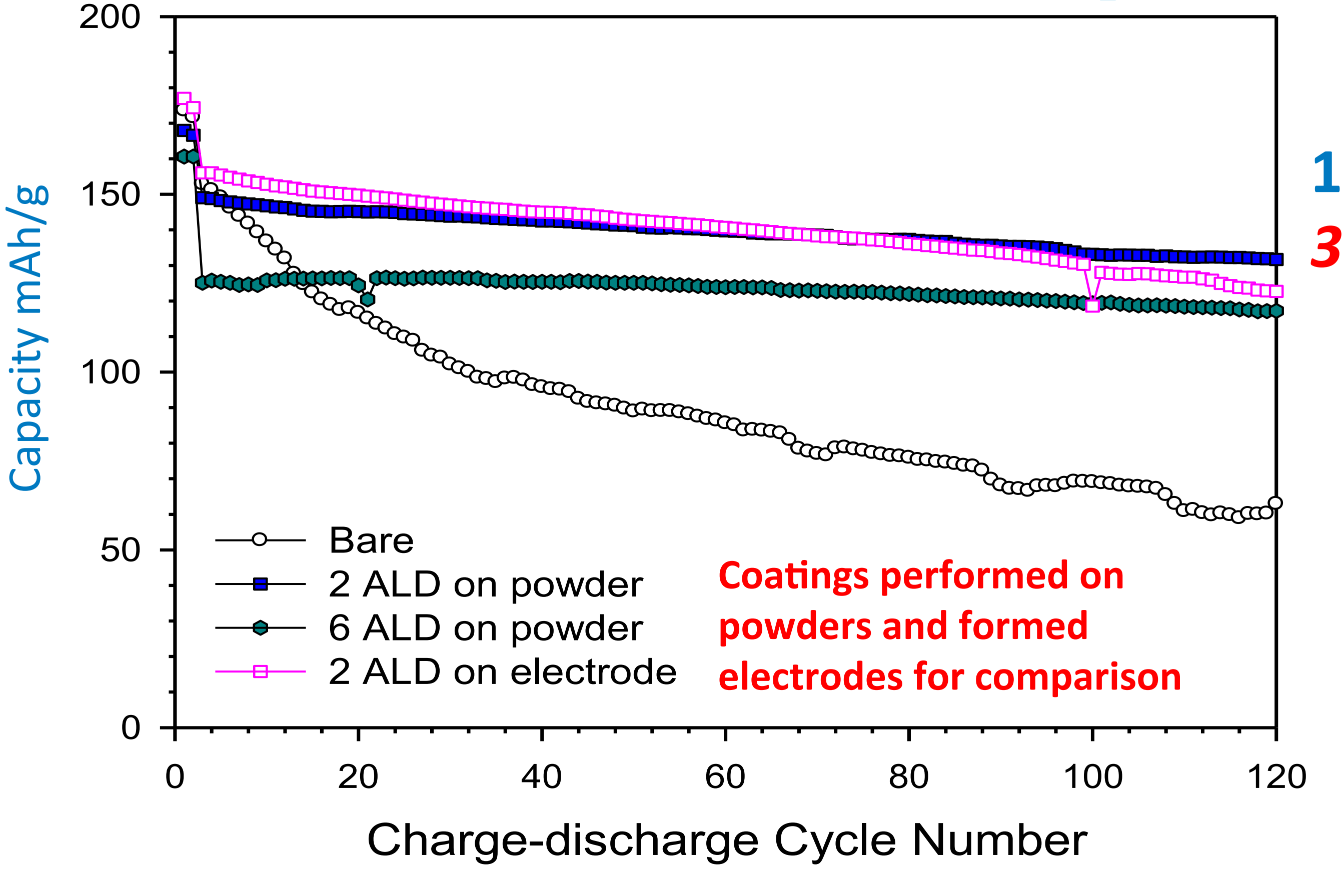


- **Conformal**
- **Monolayer thickness control (~1 Å)**
- **Especially powerful for nano-structured materials**
- **Commercially scalable** (**No solvent**, no excessive amount of precursors, No post-heat-treatment at high-temperature)
- **Here we will enable integration of "ALD-like" processes into existing battery fabrication (AP-ALD).**

A. C. Dillon, A. W. Ott, J. D. Way, S. M. George, *Surf. Sci.* **1995**, *322*, 230., S. M. George, *Chem. Rev.* **2010**, *110*, 111.

Relevance – Impact on Barriers

Cycling Performance ALD Coated $LiCoO_2$



Coatings performed on powders and formed electrodes for comparison

1 C-rate (140 mA g^{-1})

3.3-4.5 V (*vs.* Li/Li^+)

ALD coating appears to limit degradation of $LiCoO_2$ at high potential.

ALD coatings may improve abuse tolerance

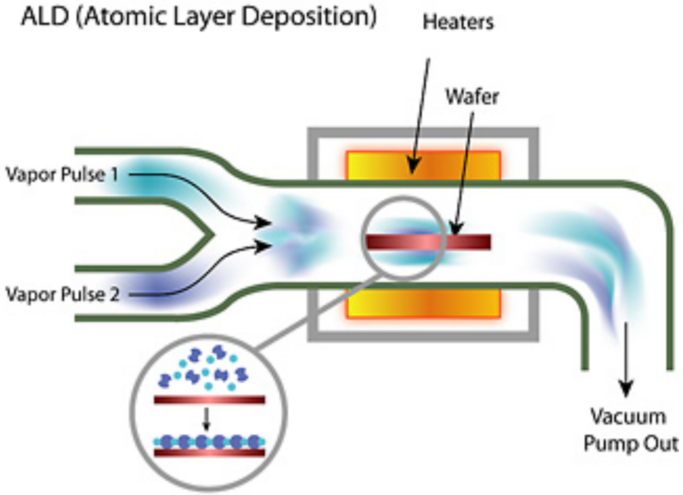
Y.S Jung, A.S. Cavanagh, Dillon A.C. Groner M.D. George S.M. and Lee, S-H. *J. Electrochemical Society* 157(2010) A75.

Milestones

Month / Year	Milestone or Go/No-Go Decision	Description	Status
FY14–Q1	Milestone	Complete construction of developmental in-line ALD depositions characterization reactor	Complete
FY14-Q2	Milestone	Demonstrate and optimize deposition of aluminum oxide on a flexible polymer films using the new in-line ALD reactor	Complete
FY14-Q3	Milestone	Complete analysis of parameters for ALD deposition onto samples of known porosity	On-going in FY15, project only partially funded in FY14
FY14-Q4	Milestone	Demonstrate coating of aluminum oxide via in-line ALD on coated cathode samples provided by ABR collaborators and submit for testing at multiple laboratories	On-going in FY15, project only partially funded in FY14
FY15-Q1	Milestone	Generation of Partnership Development Package	Complete
FY15-Q2	Milestone	Initial Development and Results for In-line ALD on Battery Electrodes	Complete
FY15-Q3	Milestone	Participate at AMR-2015	Complete
FY15-Q4	Milestone	Final report on Development of Commercialization Partner for In-Line ALD for Battery Electrode Coatings	In Progress

Current ALD Approaches

Flat Substrate Coating Reactors

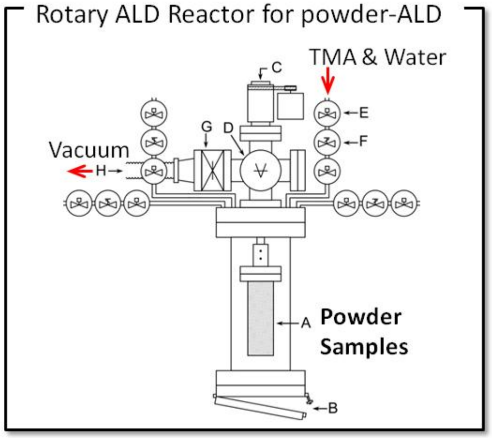


All systems currently rely on reactant exposure and extensive inert gas purging.

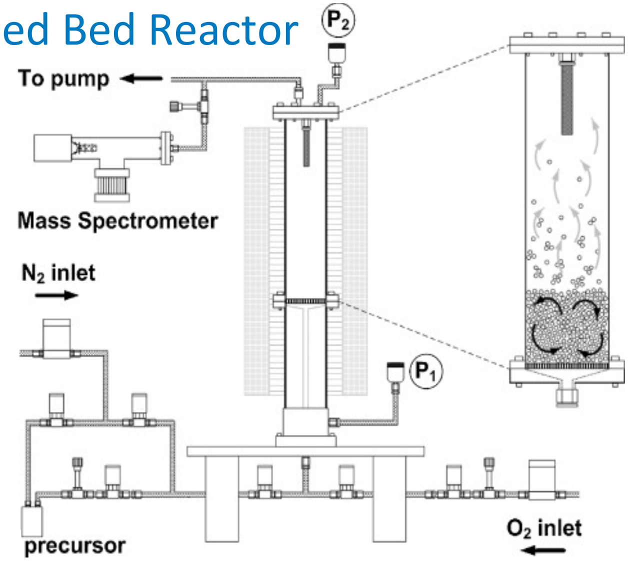
- Slow overall film growth rates
- Batch processing limitations

Particle reactors have been scaled up to kg size batches.

Particle Processing Reactors



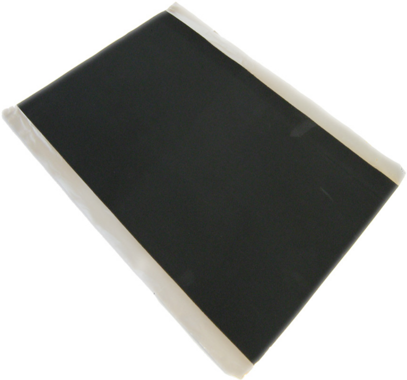
Fluidized Bed Reactor



Lithium Ion Battery Production

Aluminum Current Collector

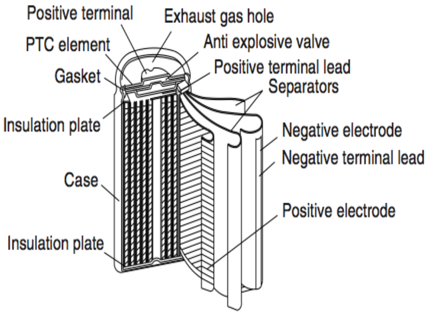
Application of Primary/Secondary Li Slurry to Al (Roll to Roll)



Calendaring material (Roll to Roll)

ALD coating will likely integrate between calendaring and winding

Winding of Cathode/Separator/Anode (Roll to Roll)



18650 Battery Assembled

Lithium ion battery manufacturing is dominated by roll to roll processing (18650 wound cell used as an example)

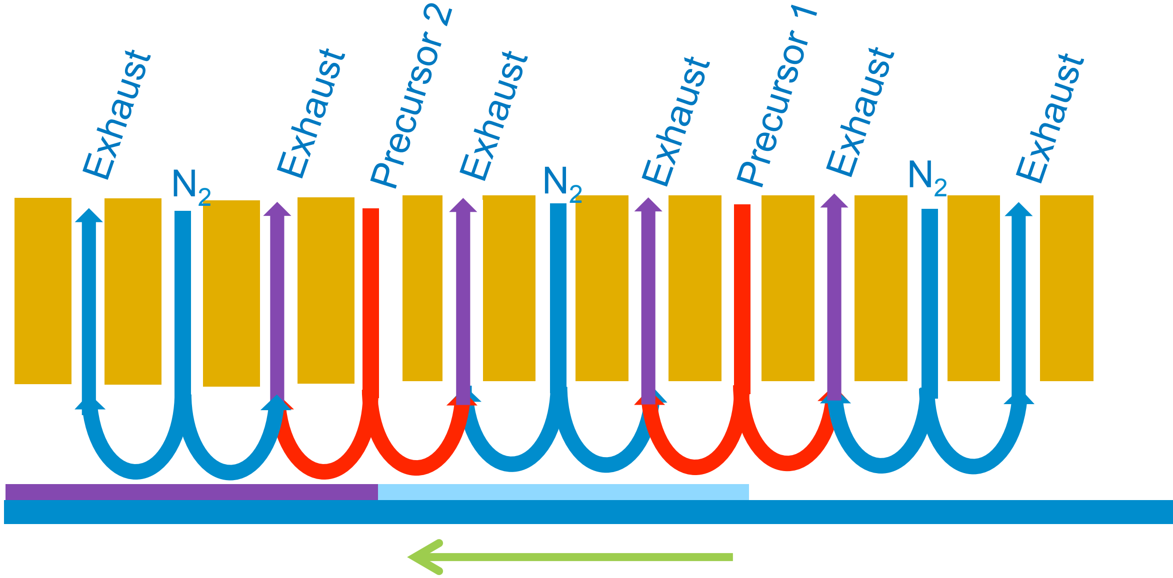
Spatial ALD for In-Line Processing

In-line ALD separates reactant exposure in space ("Spatial ALD") rather and temporally (traditional ALD)

Gas introduction manifold head contains channels for reactant precursors as well as isolation of precursors through exhaust and purge gas channels.

A virtually identical process is used for high-volume, low-cost coating deposition used in coated glass manufacturing.

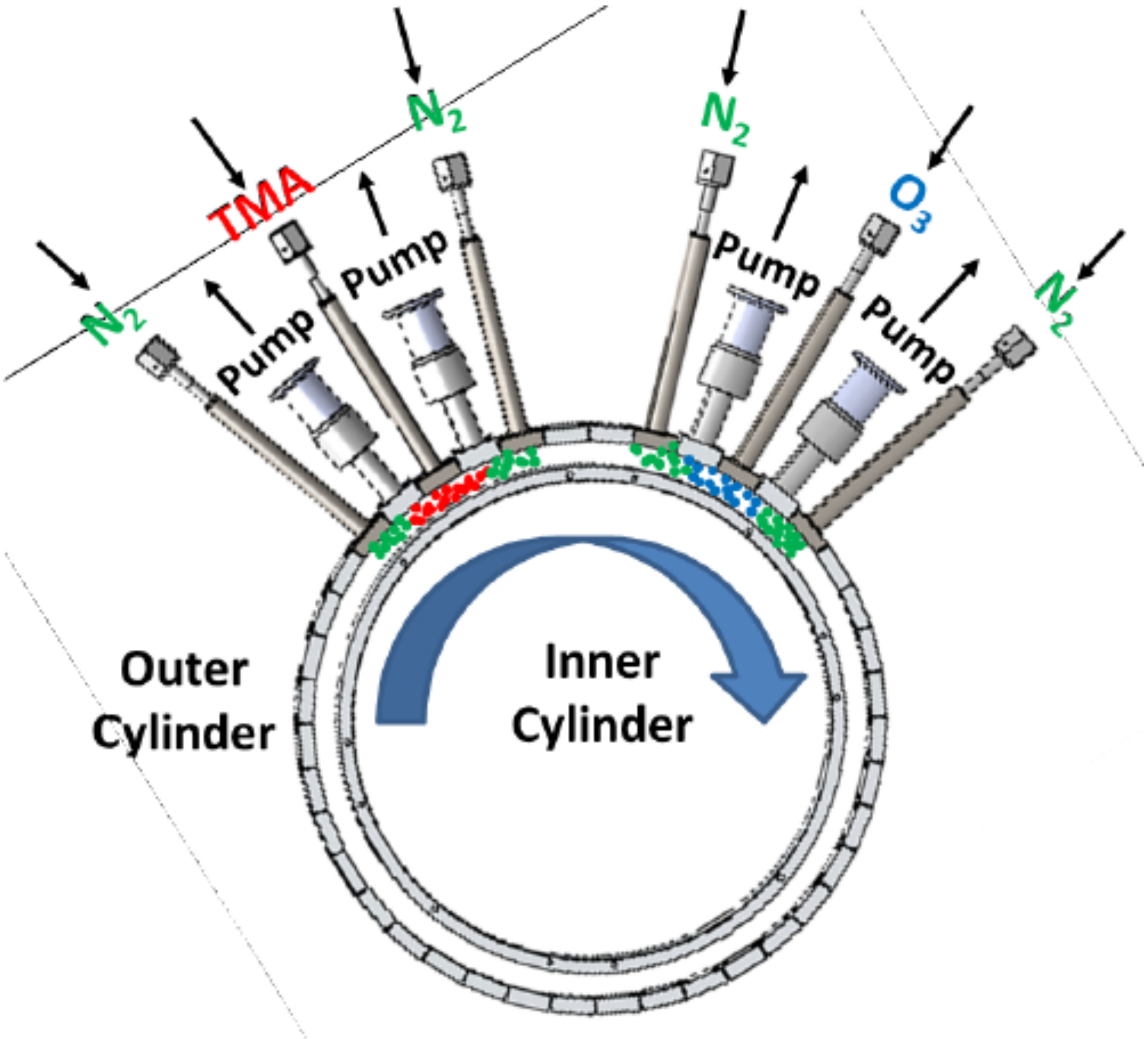
In-line AP-ALD for Manufacturing



Electrode slurry coated foil translates under multiport "AP-ALD" deposition head

Similar to known CVD based high throughput manufacturing processes

Next Generation Rotating Cylinder Reactor Concept



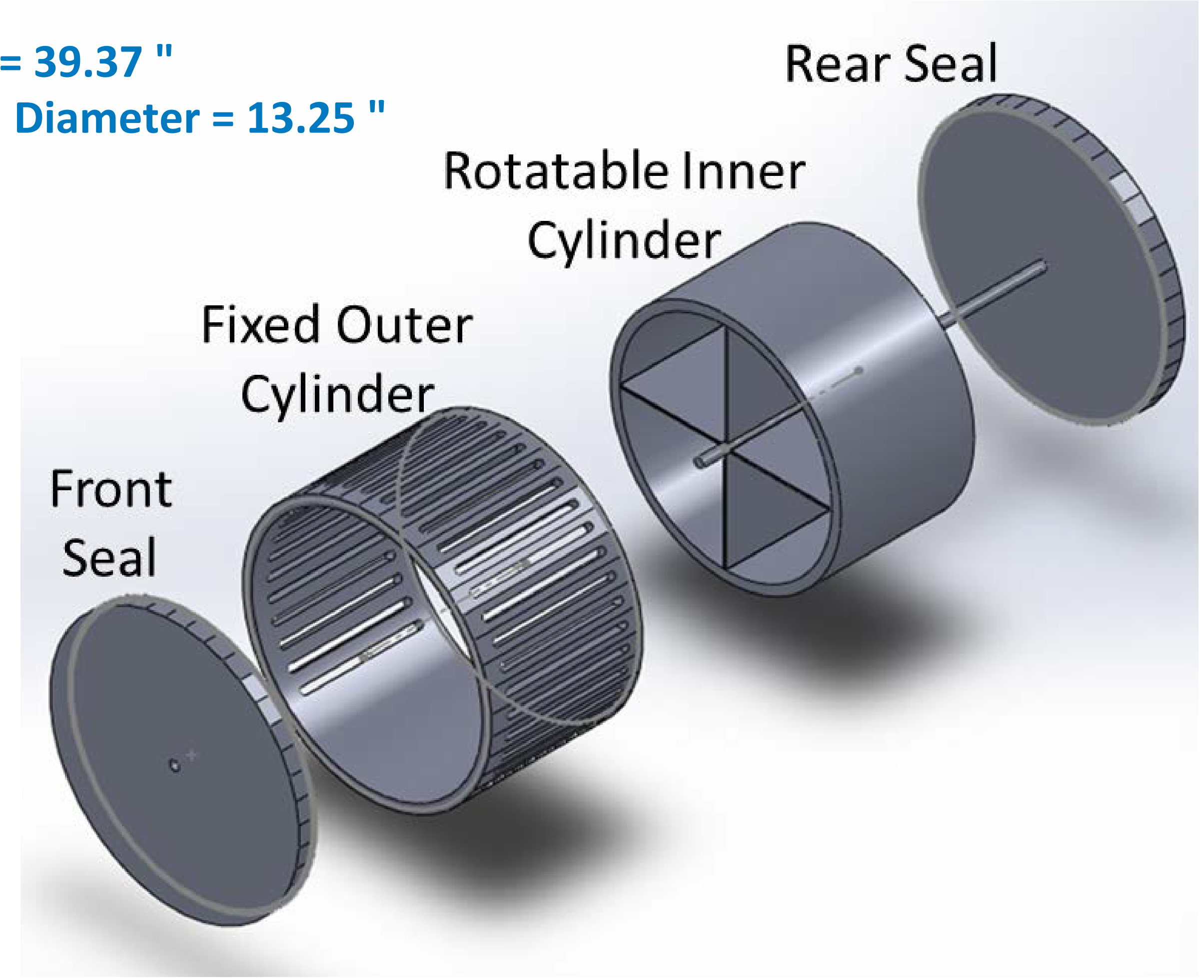
Two concentric cylinders maintain gap.

Large diameter cylinder provides greater separation between slits.

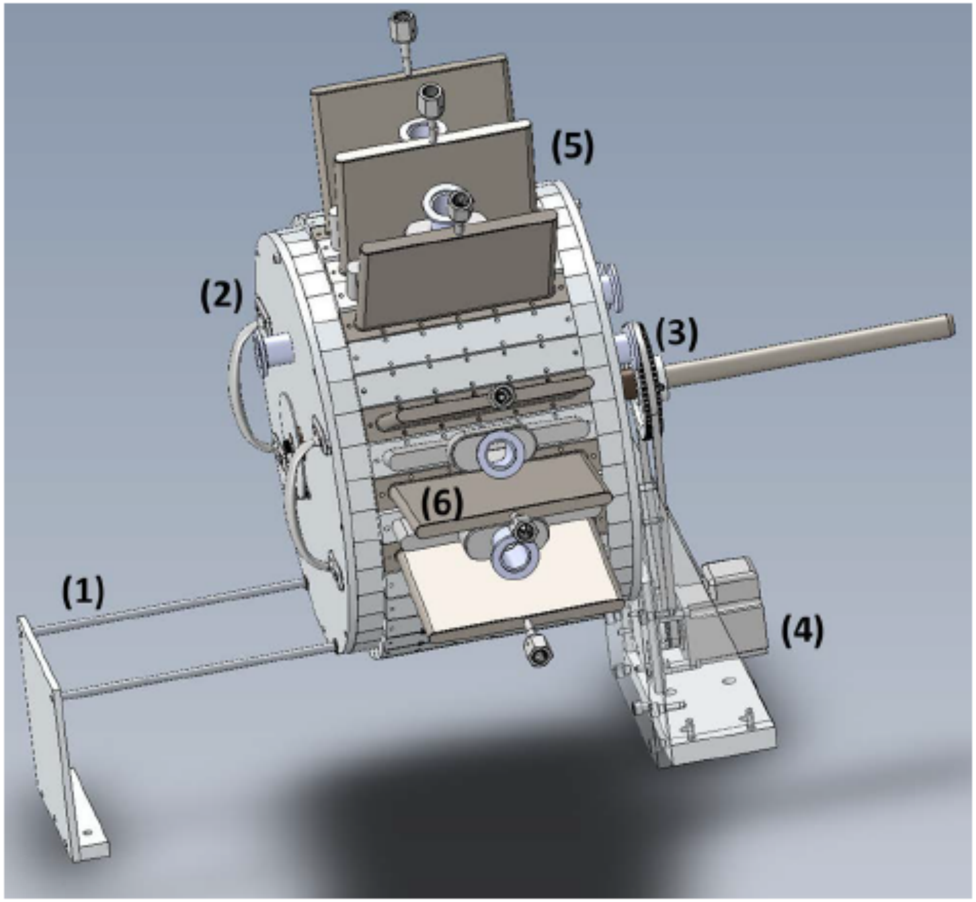
Modular design allows adjustable position for precursor, pump & purge channels.

Reactor with Rotatable Inner Cylinder & Fixed Outer Cylinder with Slits

Inner Cylinder: Diameter = 12.69"
Width = 7.75 "
Circumference = 39.37 "
Outer Cylinder: Diameter = 13.25 "



Roll to Roll S-ALD Design



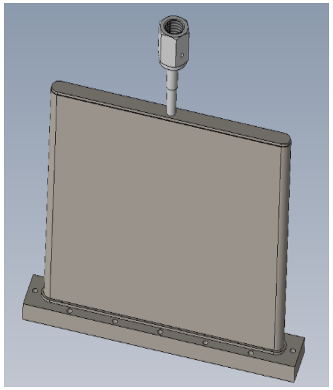
(1) Railings to move inner cylinder in & out of outer cylinder.

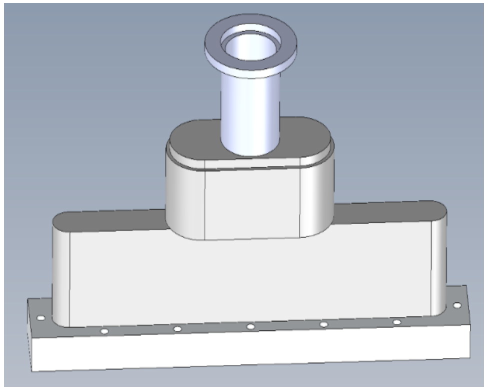
(2) Front door.

- (3) Pulley that rotates inner cylinder.
- (4) Stepper rotary motor.

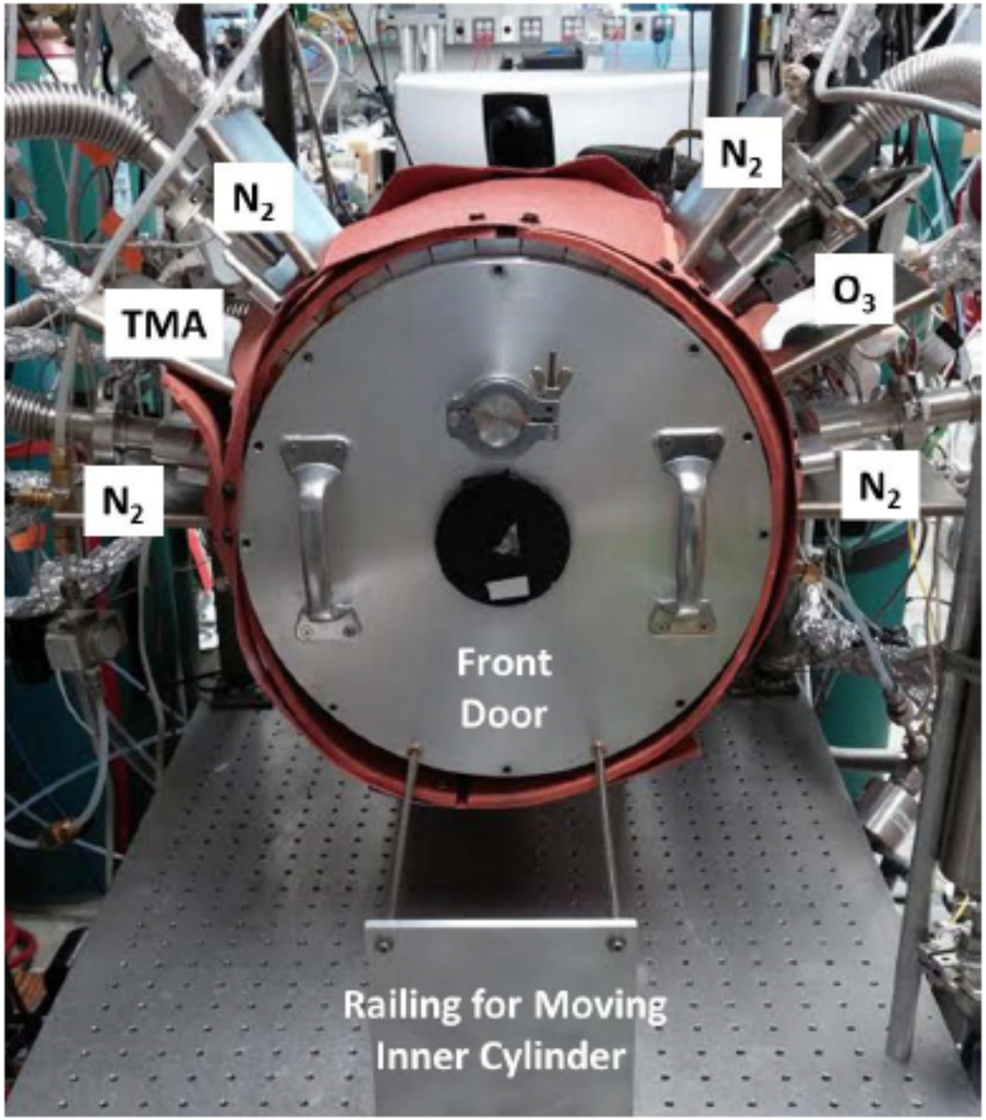
(5) First reactant zone.

(6) Second reactant zone.

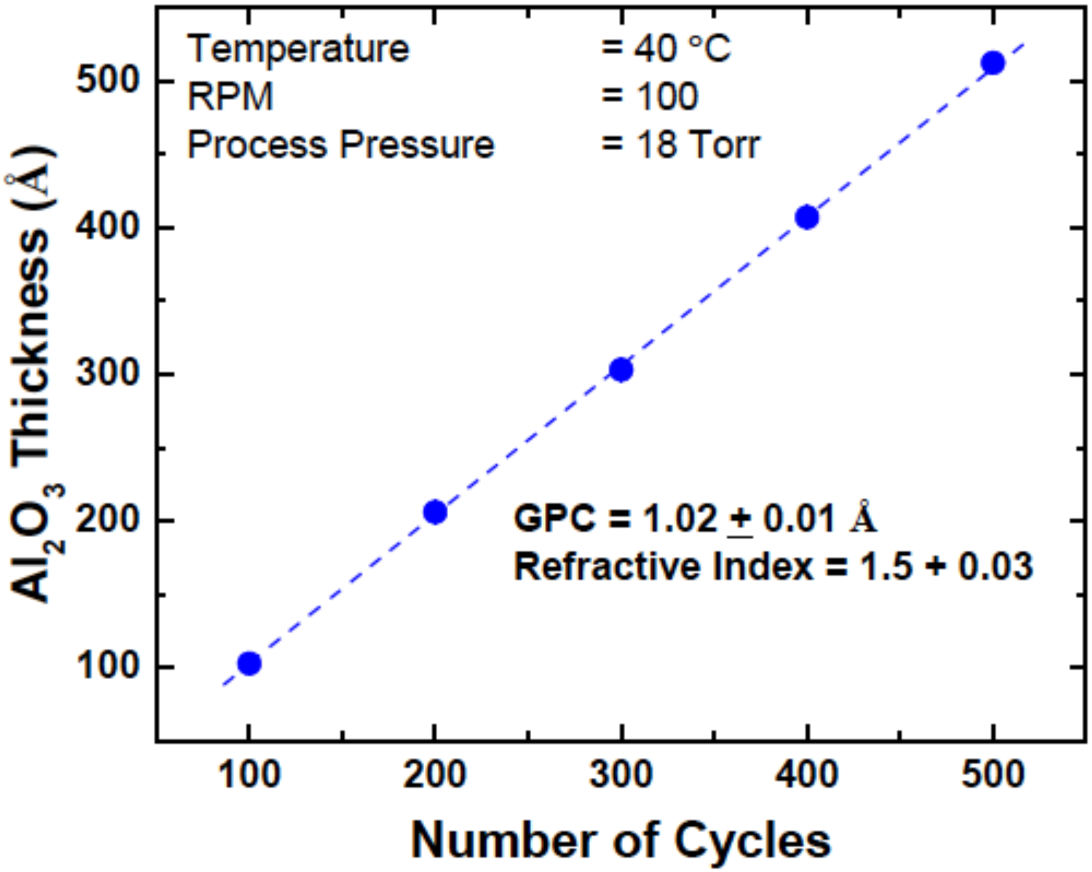

Dosing Module


Vacuum Module

Completed Reactor Configured for Al_2O_3 Deposition



Growth of Al_2O_3 ALD Films Versus Number of ALD Cycles at 100 RPM



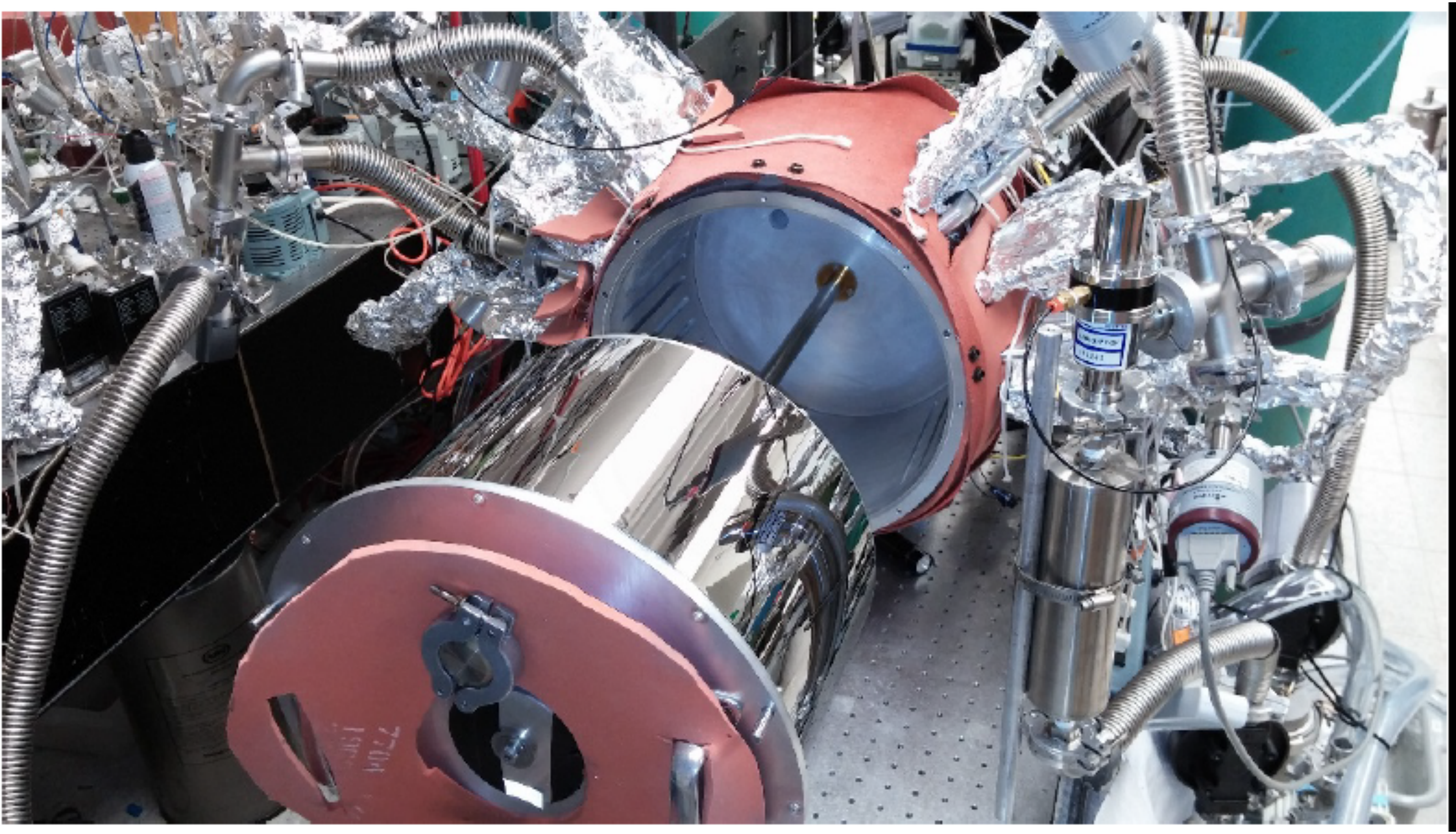
Linear growth as measured by ellipsometry

Per Cycle: Growth rate of 1.02 Å/cycle

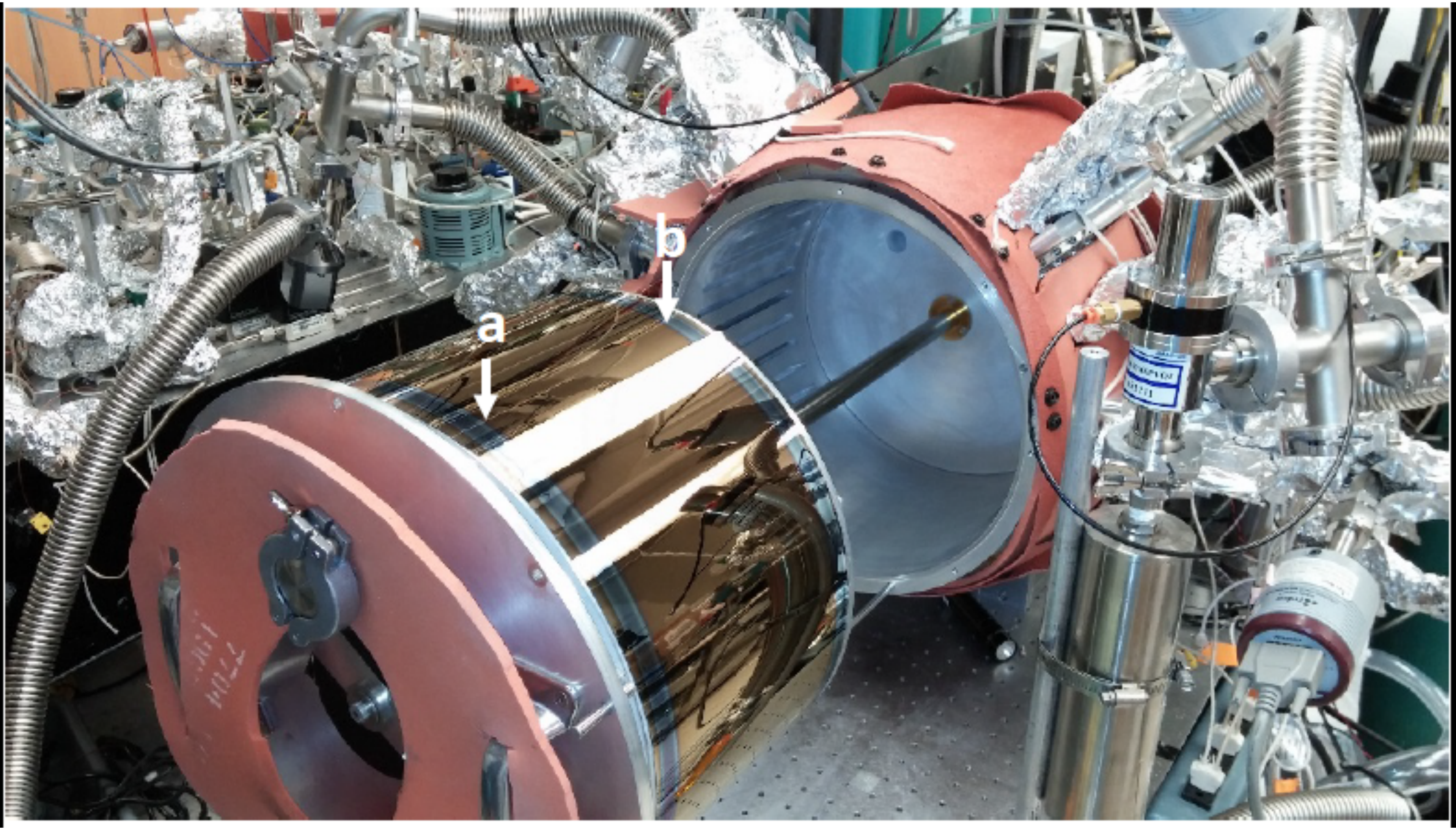
Per Time: Growth rate of 1.7 Å/s

Much higher growth rates possible

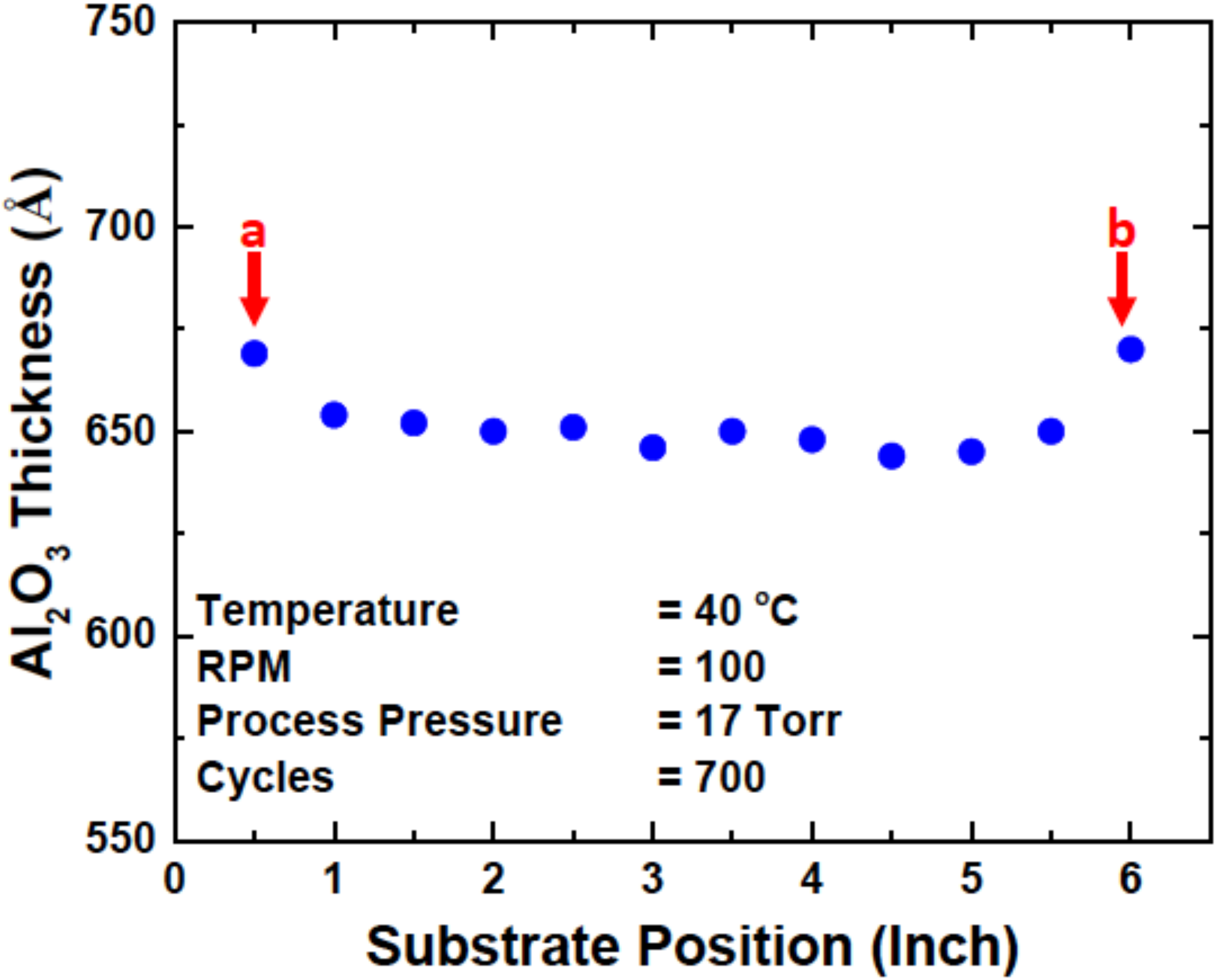
Flexible Foil Substrate Prior to Loading



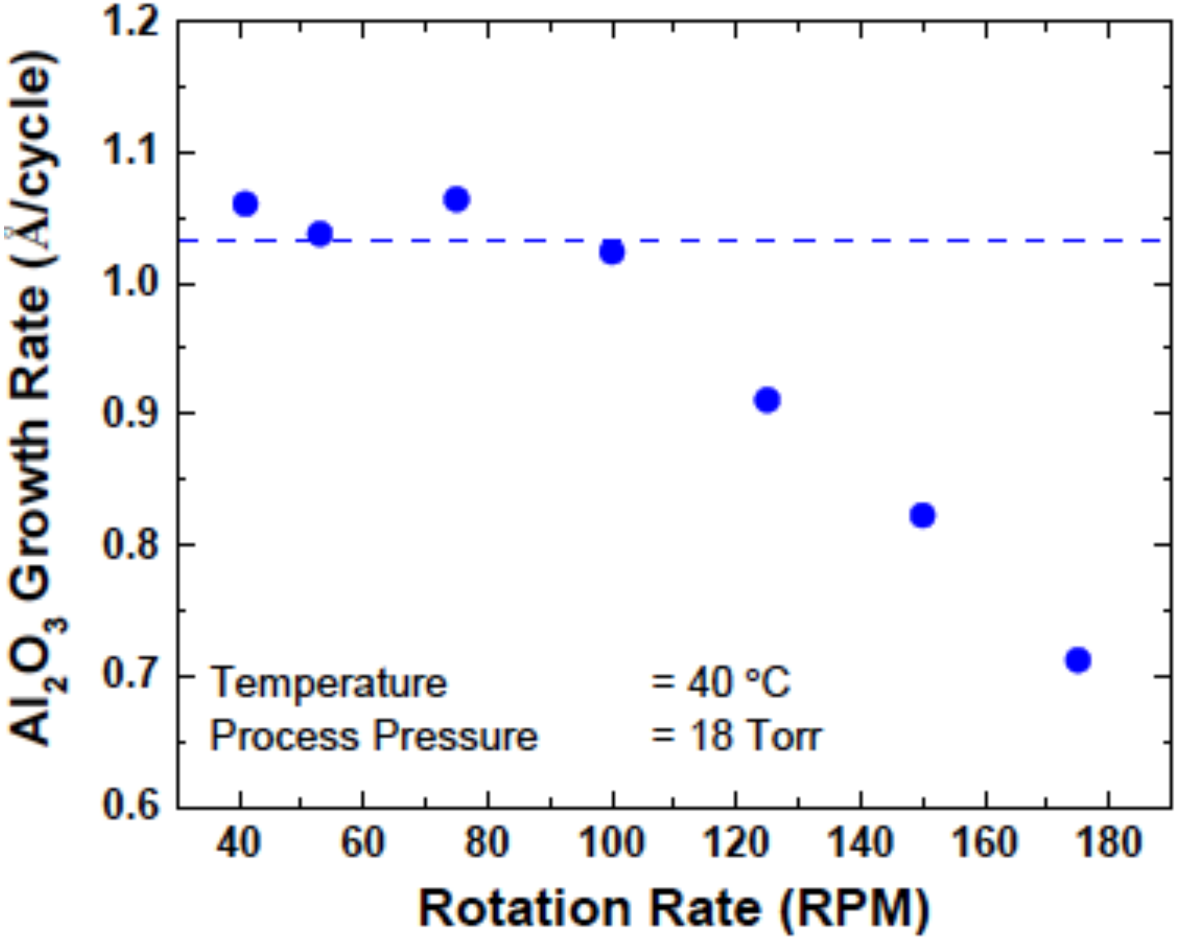
Flexible Foil Substrate Post Deposition



Sample Thickness Measured Across Substrate



Al_2O_3 Growth Rate Versus Rotation Rate at Process Pressure of 18 Torr



Growth rate constant with rotation rate until >100 RPM

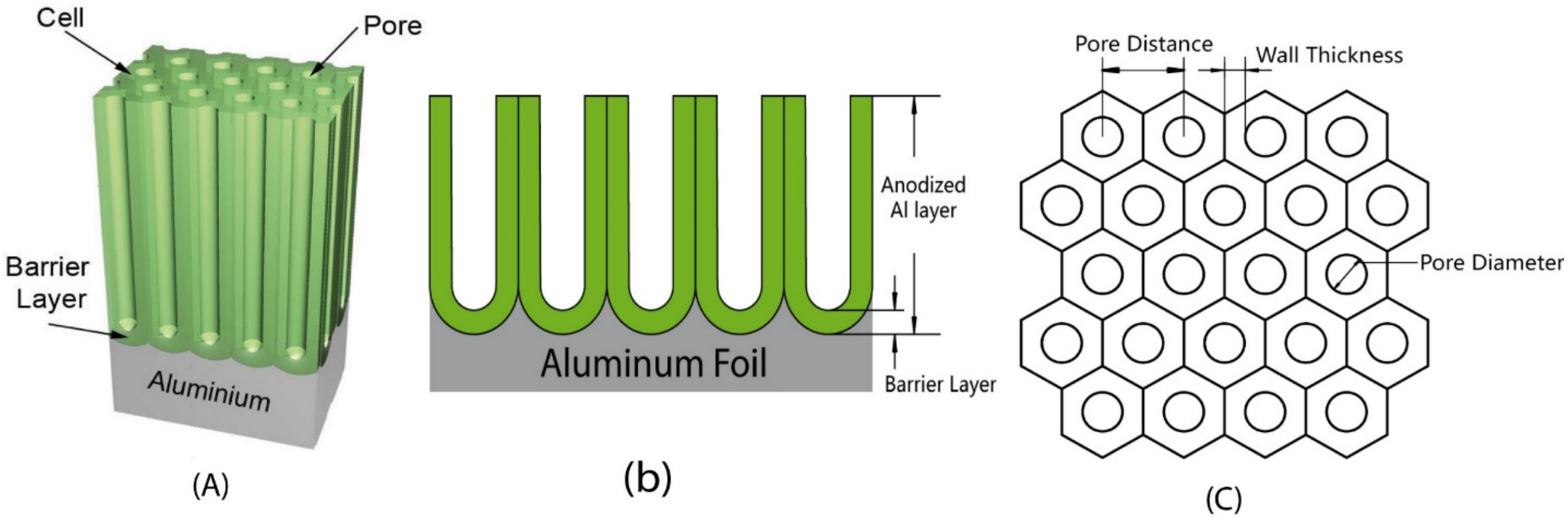
100 RPM corresponds to ~300 ft/min equivalent line speed

Growth rate constant for lower line speeds

Depositions conducted on non-porous substrates; ability to coat porous samples at speed still needs to be demonstrated

Anodic Aluminum Oxide (AAO) as Model Porous Substrate

Anodic aluminum oxide (AAO) films are being used as model porous substrates to characterize the ability to conformally coat porous films at varied processing conditions

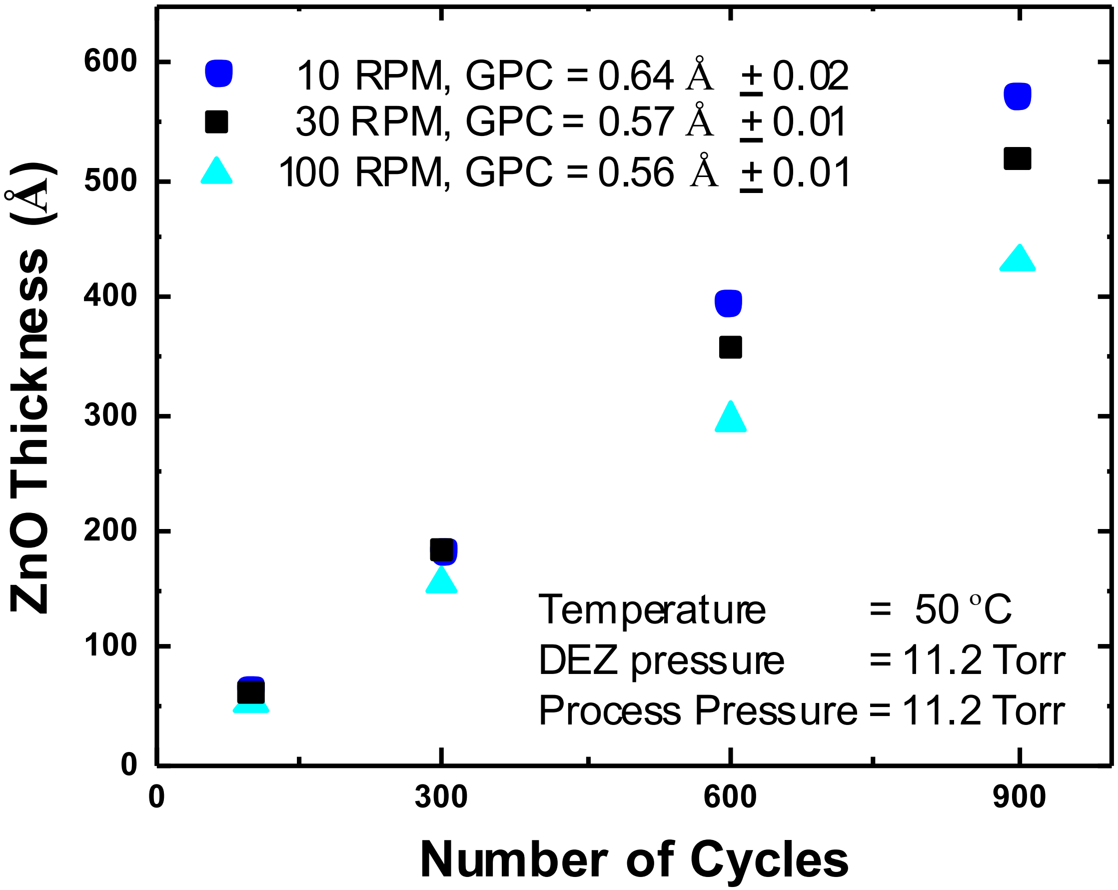


AAO films consist of arrays of well defined and uniform pore diameters that can be varied in a controlled fashion. This enables AAO to serve as an ideal substrate for identifying suitable processing conditions for coating known pore sizes at varied processing conditions.

ZnO ALD on Flat Metal-Coated Flexible PEN Substrates

In order to accurately assess the ability to coat porous AAO samples, we adapted and ALD process for deposition of ZnO.

This enabled use of standard materials analysis methods to differentiate the deposited material from the base substrate.



Experimental Matrix for Assessment of Porous Coverage

Initial Conditions: Revolutions per Minute (RPM) & AAO Pore Diameters

Pore Diameter = 50 nm	Pore Diameter = 100 nm	Pore Diameter = 150 nm
10 RPM	10 RPM	10 RPM
30	30	30
100	100	100
150	150	150
200	200	200

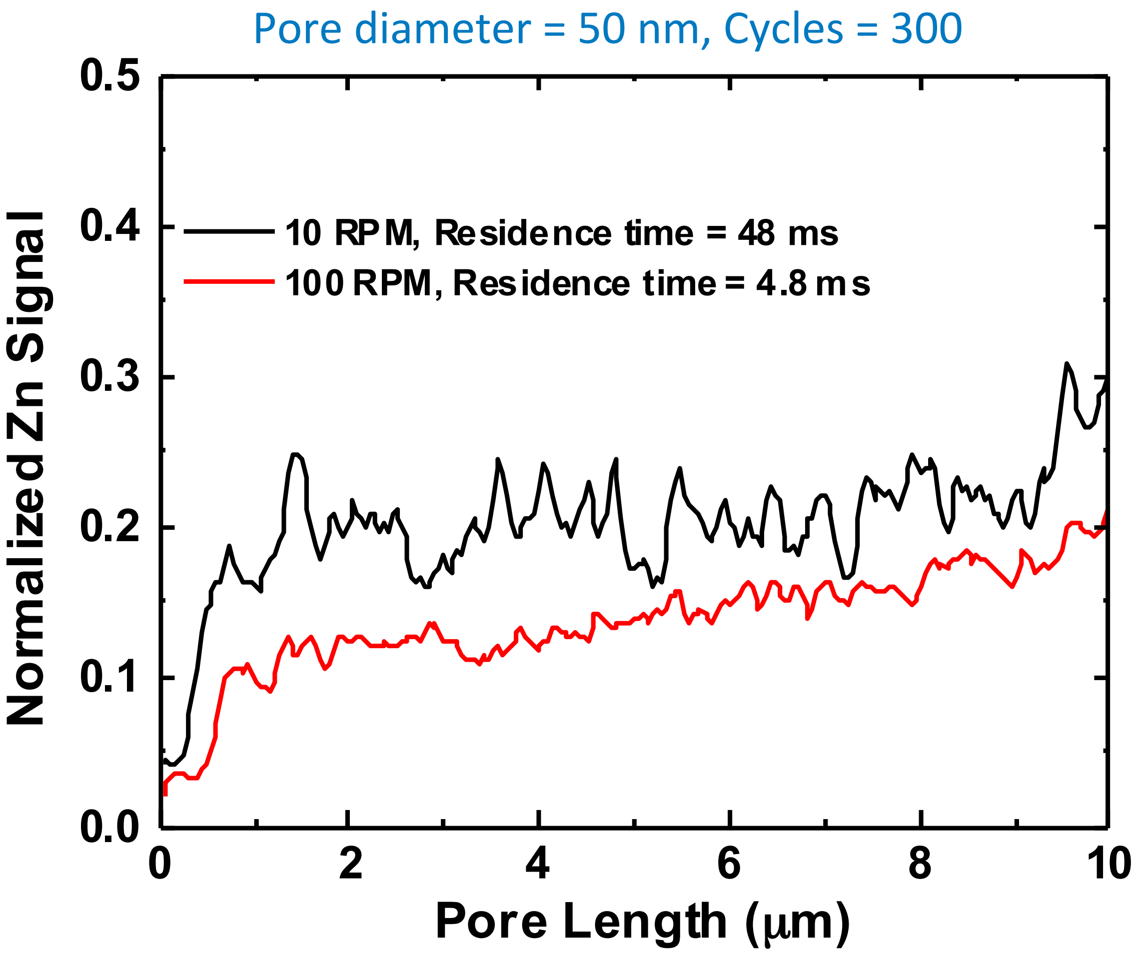
Length of pores in AAO membrane = 10 µm. Samples prepared by Dmitri Routkevitch at InRedox.

Experimental Measurement of Coating Across Pore Structures

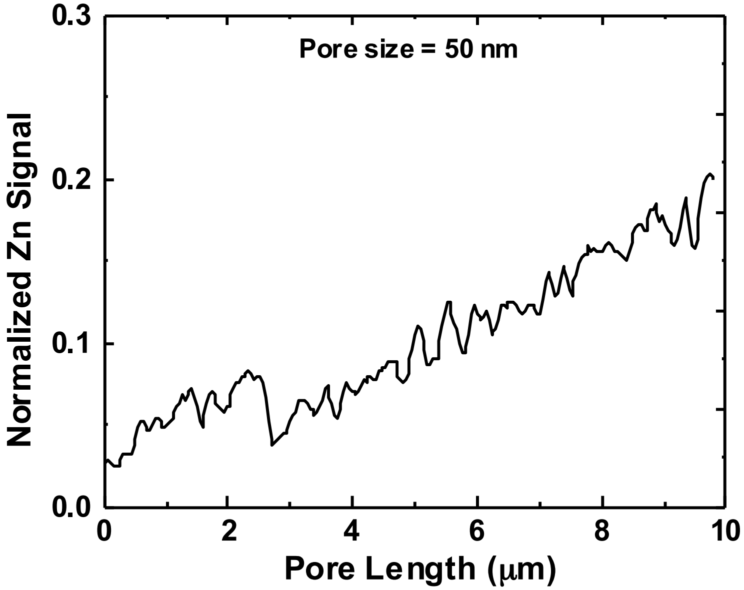
Energy Dispersive X-ray Spectroscopy (EDX) was used to detect the presence of Zn across the cross-sectional length of porous AAO films following deposition.

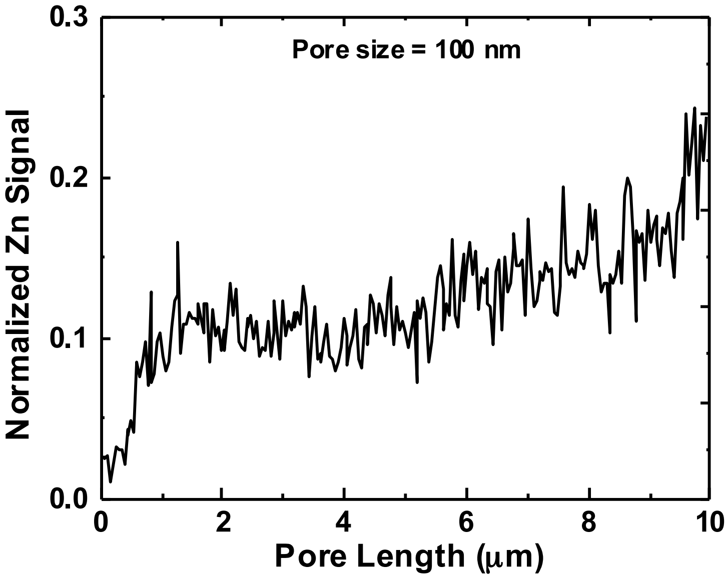
A straight line across the film profile gives preliminary indication of uniform pore coverage.

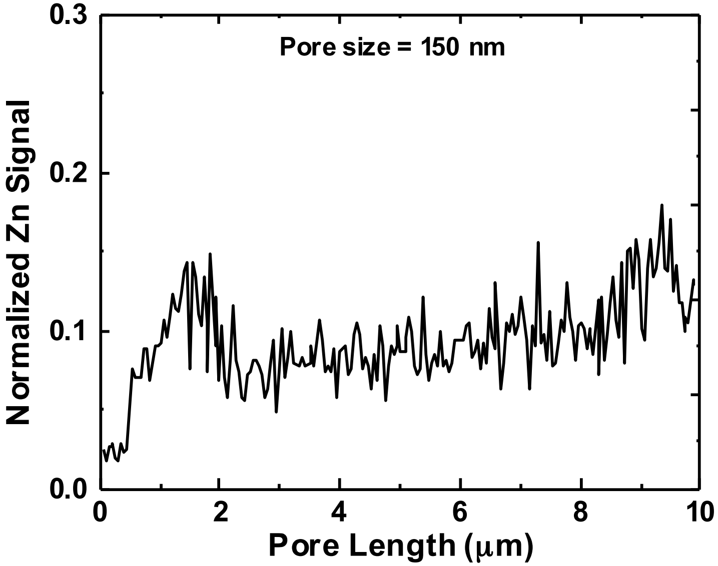
Further experiments being conducted to more accurately assess conformality of coating.



RPM = 200, Cycles = 600 for Various Pore Diameters







Uniformity of Zn signal across pore structures clearly varies as a function of pore size indicating limitation of given processing conditions for effectively coating small sizes.

Note that the effective line speed for this process would be approaching ~600 ft/min. Decreased line speeds enable more uniform coating.

Response to Previous Year Reviewers’ Comments

This project was not reviewed in FY 14

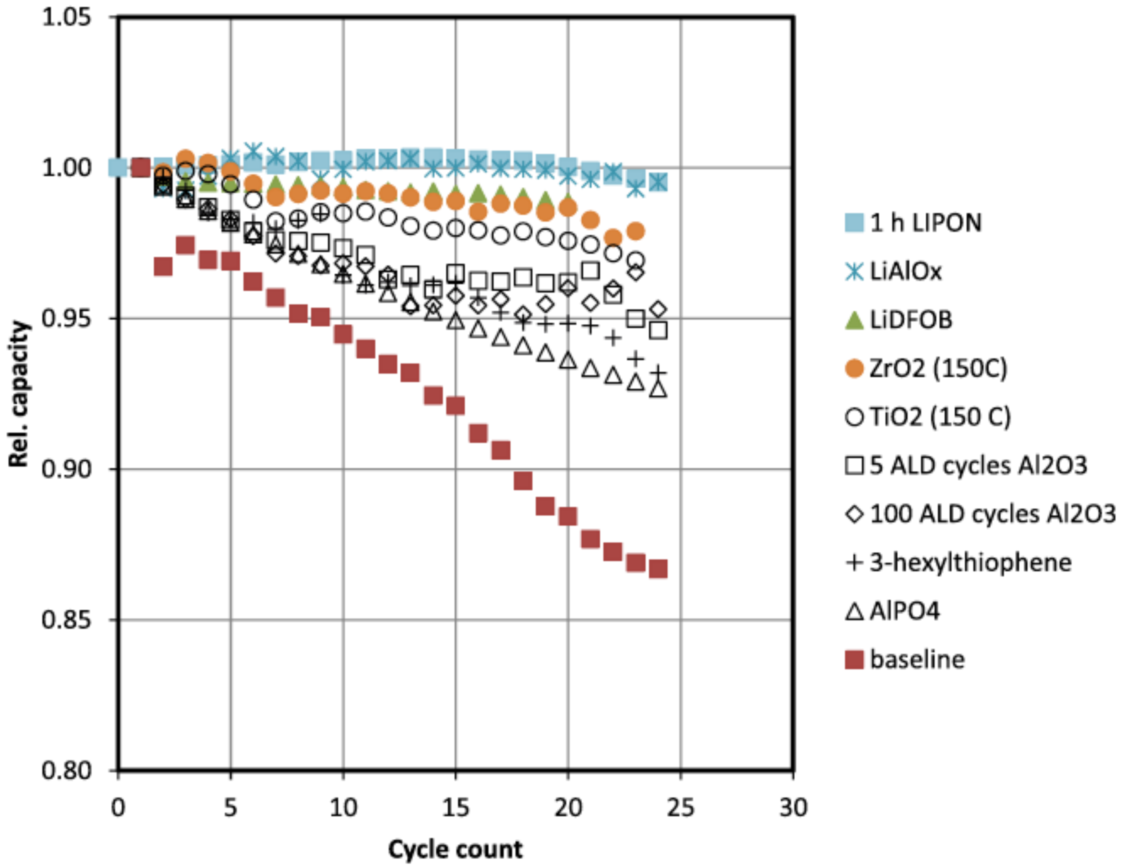
Collaboration and Coordination with Other Institutions

In addition to our collaboration with CU-Boulder, in FY14, NREL collaborated with ANL and ORNL to help determine the causes of voltage fade in the HE5050 material.

NREL provided ALD coated materials and conducted joint analysis of coated and uncoated samples with the other laboratories.

This collaborative effort demonstrated that while coatings improve capacity fade, there was no measureable effect of coatings in the voltage fade issues.

Bloom et al. Journal of Power Sources, 249, 2014, 509-514



In FY15, NREL is continuing our partnerships with ANL and ORNL to further development of high energy – high voltage cell chemistries.

Remaining Challenges and Barriers

- Further experiments will be conducted to more thoroughly characterize the ability to coat porous substrates at high line speeds.
- We are currently testing both anode and cathode materials coated on our in-line reactor system to compare to previous data for coatings performed in our static deposition systems.
- Continued sample exchange, coating and testing will be conducted across our and our partners laboratories to understand impact of in-line ALD coatings on performance of a variety of cells.
- NREL will seek out additional partners to help integrate in-line coating into future manufacturing capabilities.

Proposed Future Work

- NREL will continue to partner with other VTO funded laboratories and additional collaborators to develop and test electrode and electrode materials coatings.
- NREL and CU-Boulder will continue collaboration to develop additional processing capabilities for in-line ALD coatings including transfer to a roll-to-roll capability for the existing reactor.
- NREL will seek out further industrial partnerships to integrate in-line coating in demonstration manufacturing processes.

Summary

- NREL and CU-Boulder successfully completed design and construction of a demonstration reactor for in-line rotary ALD.
- Initial deposition of aluminum oxide was accomplished at diffusion limited rates under optimized conditions.
- Deposition of aluminum oxide on flat, flexible substrates was demonstrated and showed no degradation in deposition rate for effective line speeds up to ~300 ft/min.
- Initial characterization of ALD coating on model porous substrates (AAO) was performed using ZnO deposition.
- Data to date indicates uniform coatings of porous substrates is feasible under a variety of conditions, however the team continues to explore the limits of this capability.
- Initial coatings of aluminum oxide on coated electrode foils using the in-line reactor system have been performed and are under test.
- NREL will continue to develop our methods to transfer this technology into manufacturing and to continue support of our ABR program partners.