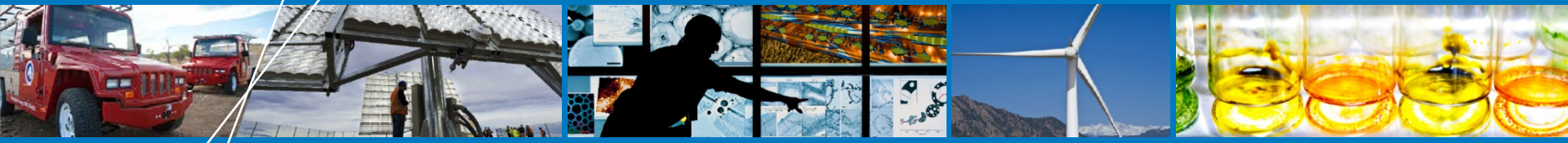
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

2012 DOE Vehicle Technologies Program Review



ES#162: Development of Industrially Viable Electrode Coatings

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This presentation does not contain any proprietary, confidential or otherwise restricted information

Project Overview

Timeline

- Project Start Date: 12/2011
- Project End Date: 12/2015
- Percent Complete: ~10%

Barriers

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

Budget

- Total Project Funding: $1.5M
- DOE Share: $1.5M
- Contractor Share: N/A
- FY11 Funding: N/A New Award
- Funding for FY12: $300K
- FY13 Anticipated Funding: $400K

Partners

- NREL (Lead)
- University of Colorado – Boulder
- Sandia NL
- Argonne NL Cell Fabrication Facility

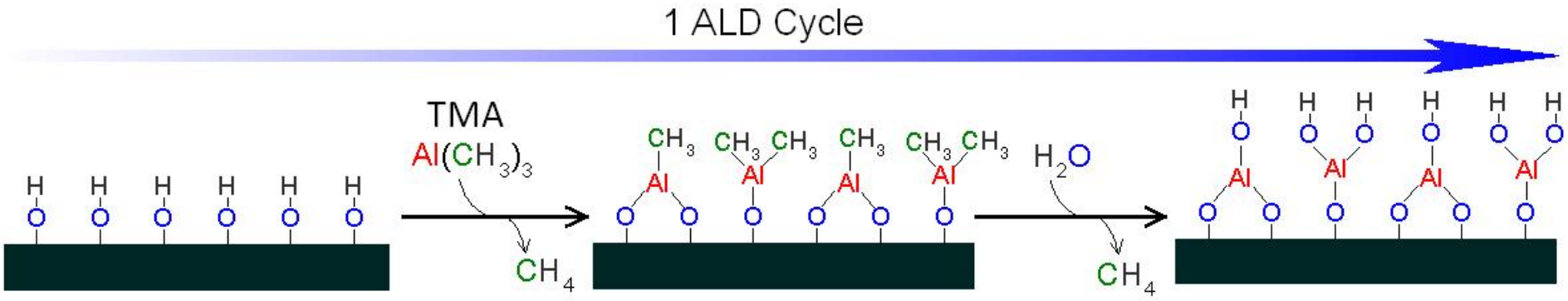
Relevance - Objective

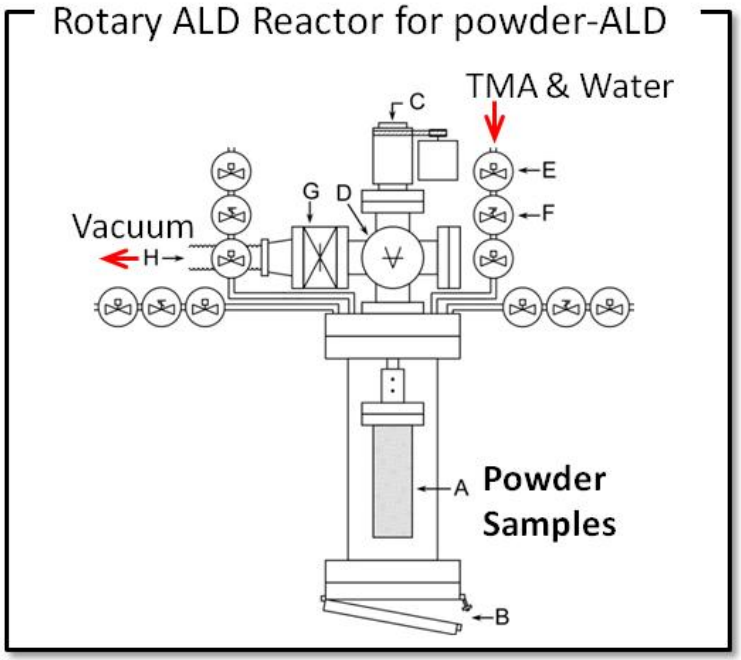
Project Objective

To develop a deposition system for 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.

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

Sequential & self-limiting surface reactions:



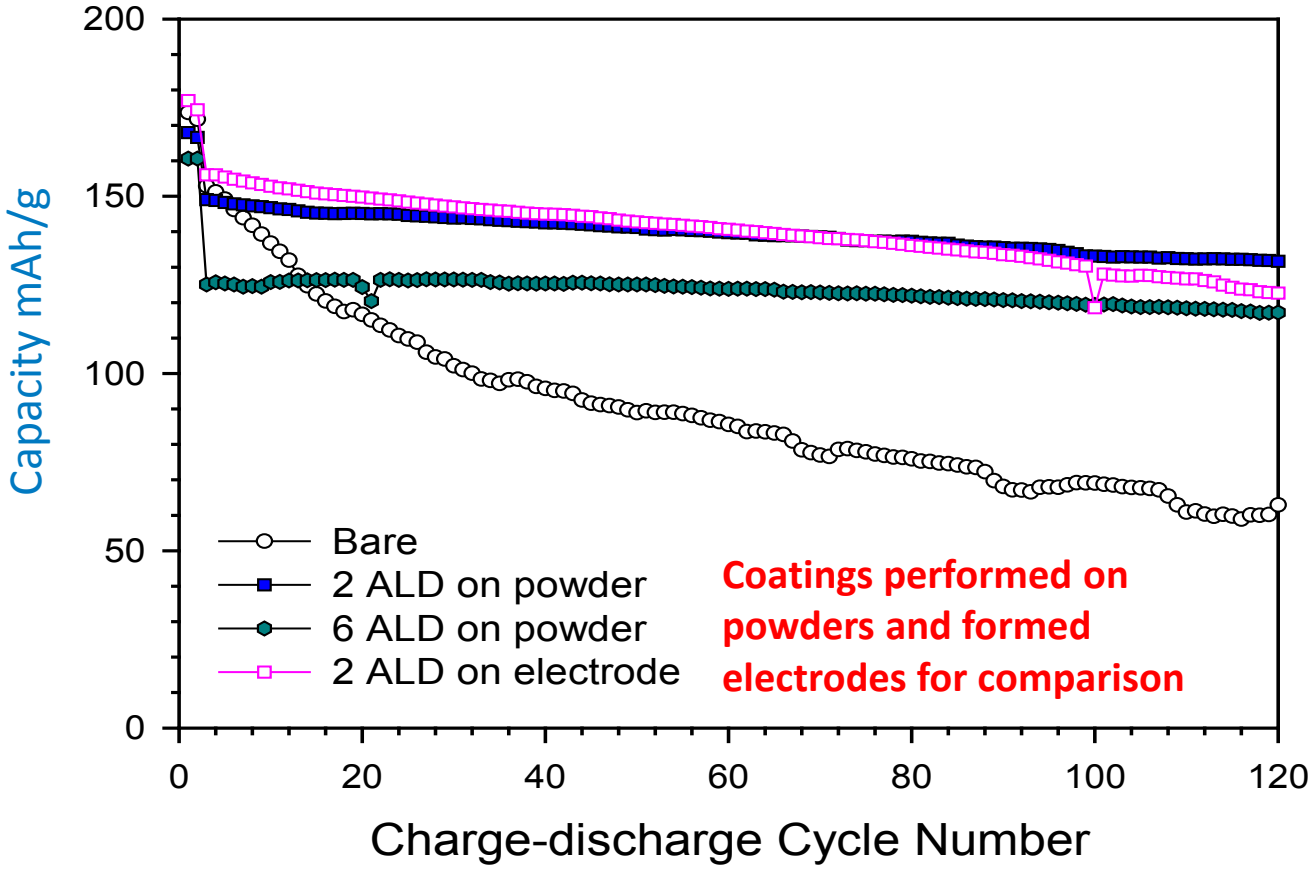


- **Conformal**
- **Atomic thickness control (~1 Å)**
- **Especially powerful for nano-structured materials**
- **Commercially scalable (No solvent**, no excessive amount of precursors, No post-heat-treatment at high-temperature)
- **Here we will enable integration of "ALD-like" processes into existing battery fabrication processes (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 $LiCoO_2$



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

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

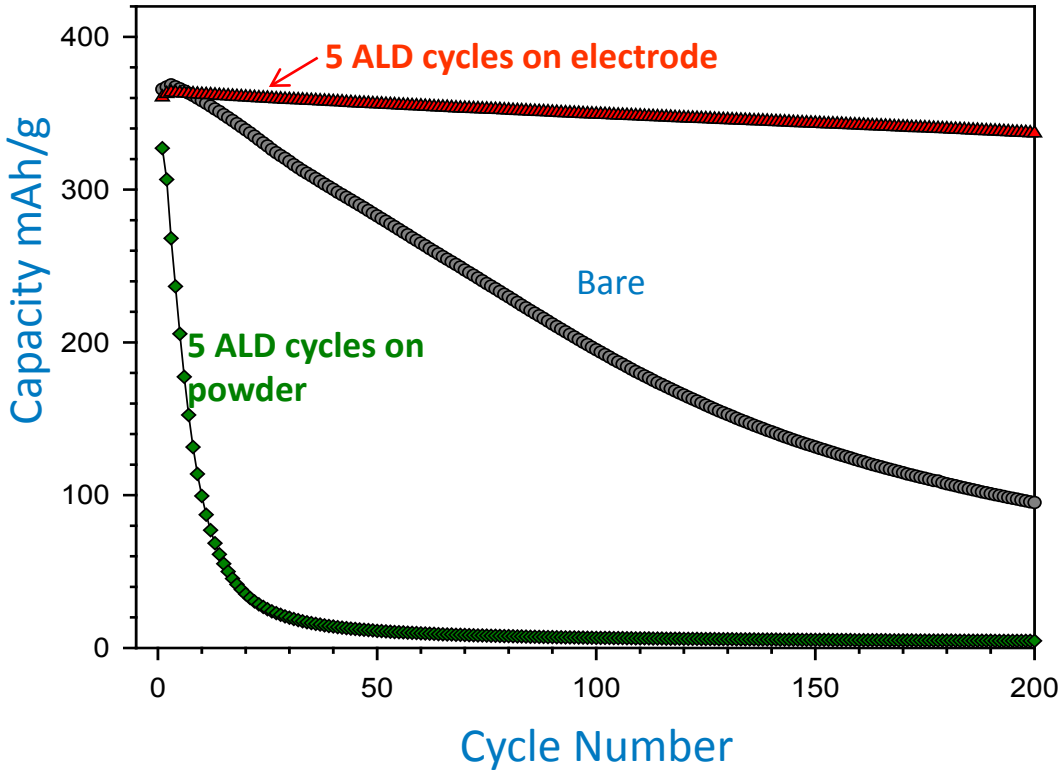
ALD coating appears to limit degradation of $LiCoO_2$ at high potential.

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.

Relevance – Impact on Barriers

Cycling Performance of Natural Graphite (NG) at 50˚C



Non-Battery Grade NG Cycling at 50˚C

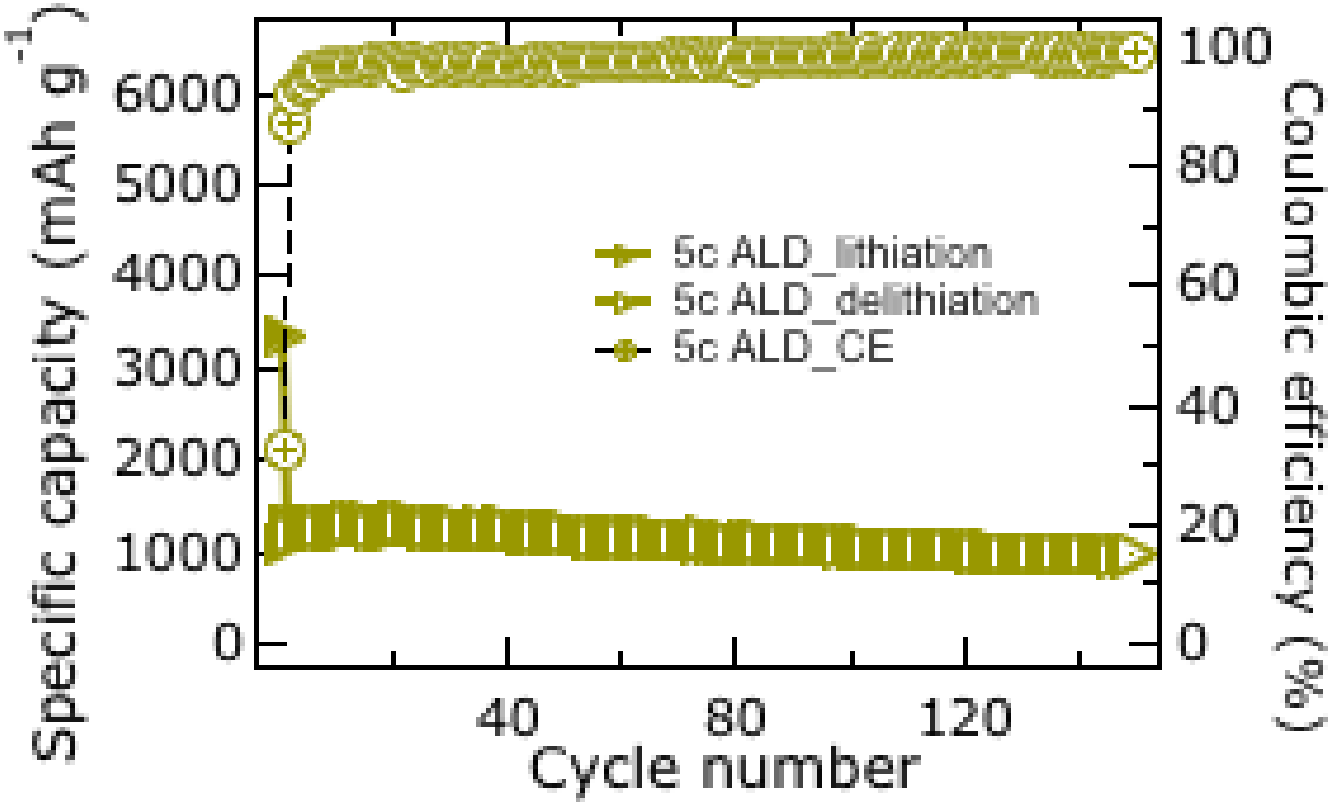
Cycling at High Temperature Generally Leads to Rapid Capacity Fade.

ALD coatings may allow stable performance at increased temperature.

Y.S. Jung, A.S. Cavanagh, L.A. Riley, S-H.. Kang, A.C. Dillon, M.D. Groner, S.M. George and S-H. Lee *Advanced Materials* 22 (2010) 2172.

Relevance – Impact on Barriers

ALD Al_2O_3 was Demonstrated to Stabilize Si/Cu Electrodes

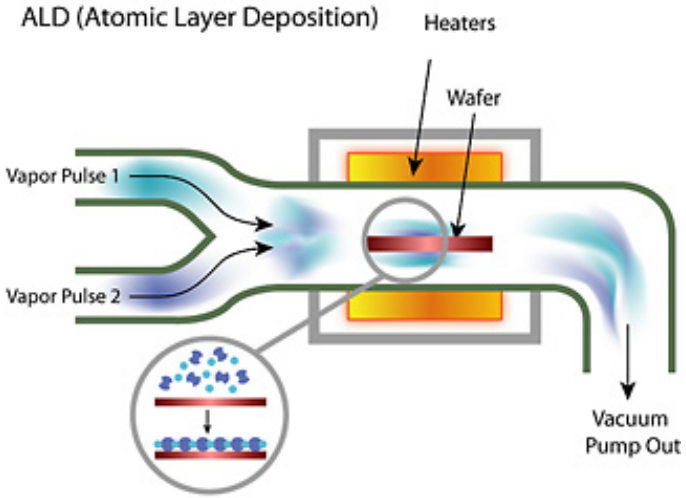


5 cycles of ALD Al_2O_3 (~1 nm) was found to be the optimal coating thickness. Capacity of Si is *constrained* to ~1000 mAh/g, but the Coulombic efficiency is improved to > 99%.

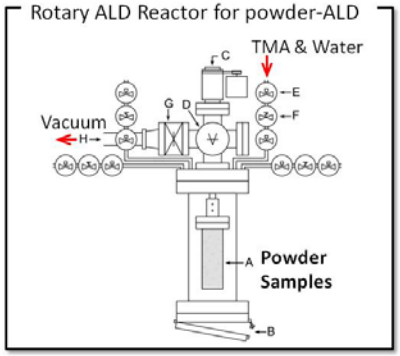
ALD coatings may improve next generation materials

Relevance - Demonstrate "ALD-Like" Techniques: Atmospheric Processing-ALD (AP-ALD) for Battery Industrial Fabrication Lines

Present ALD capabilities

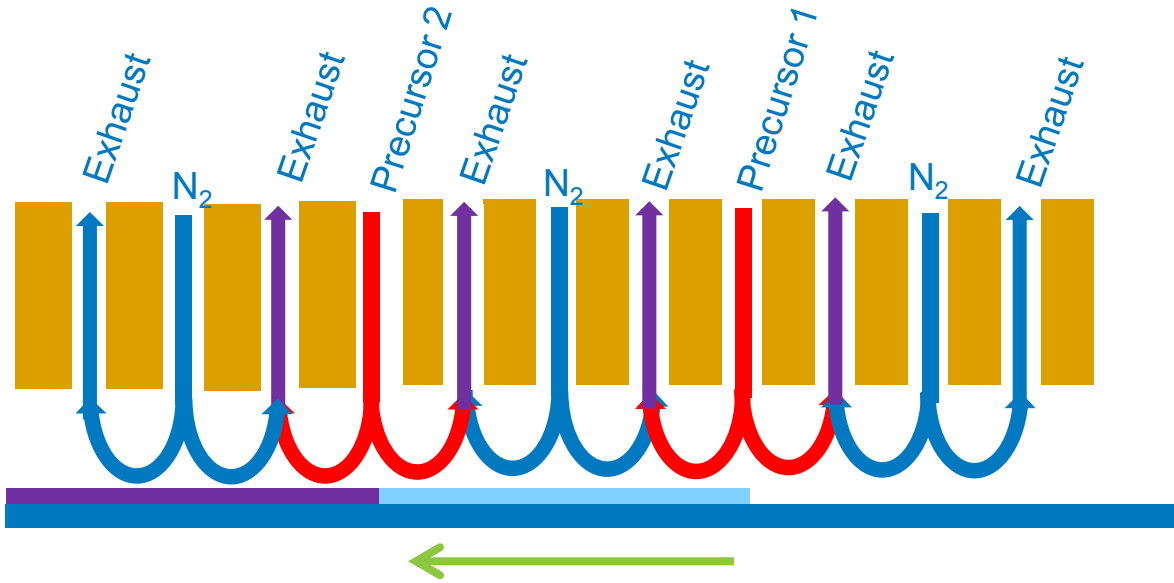


Multiple sequential exposures to formed electrode performed in single chamber at mildly reduced pressures.



In-line ALD for Manufacturing

Similar to known CVD based high throughput manufacturing processes:



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

Milestones

Date Due	Milestone	Status
May 2012	Demonstration of an Al_2O_3 ALD coating showing improved performance for a commercially viable cathode material.	On-Schedule
September 2012	Establish a deposition system capable of in-line AP-ALD on at least 6” by 6” up to 12” by 12” substrates.	On-Schedule

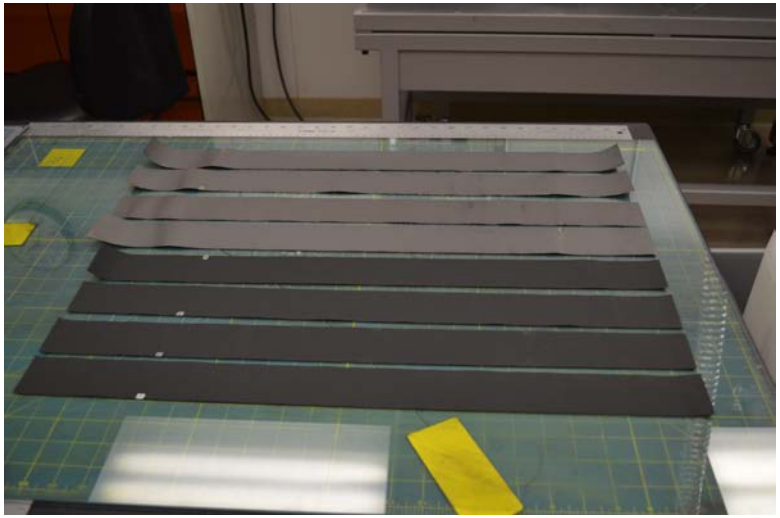
Technical Accomplishments and Progress: Coating Commercially Viable Electrode Materials

Modified rotary ALD reactor was used to coat formed electrodes of commercial materials for larger format testing.

Toda NMC(111) and Conoco Philips A10 Graphite

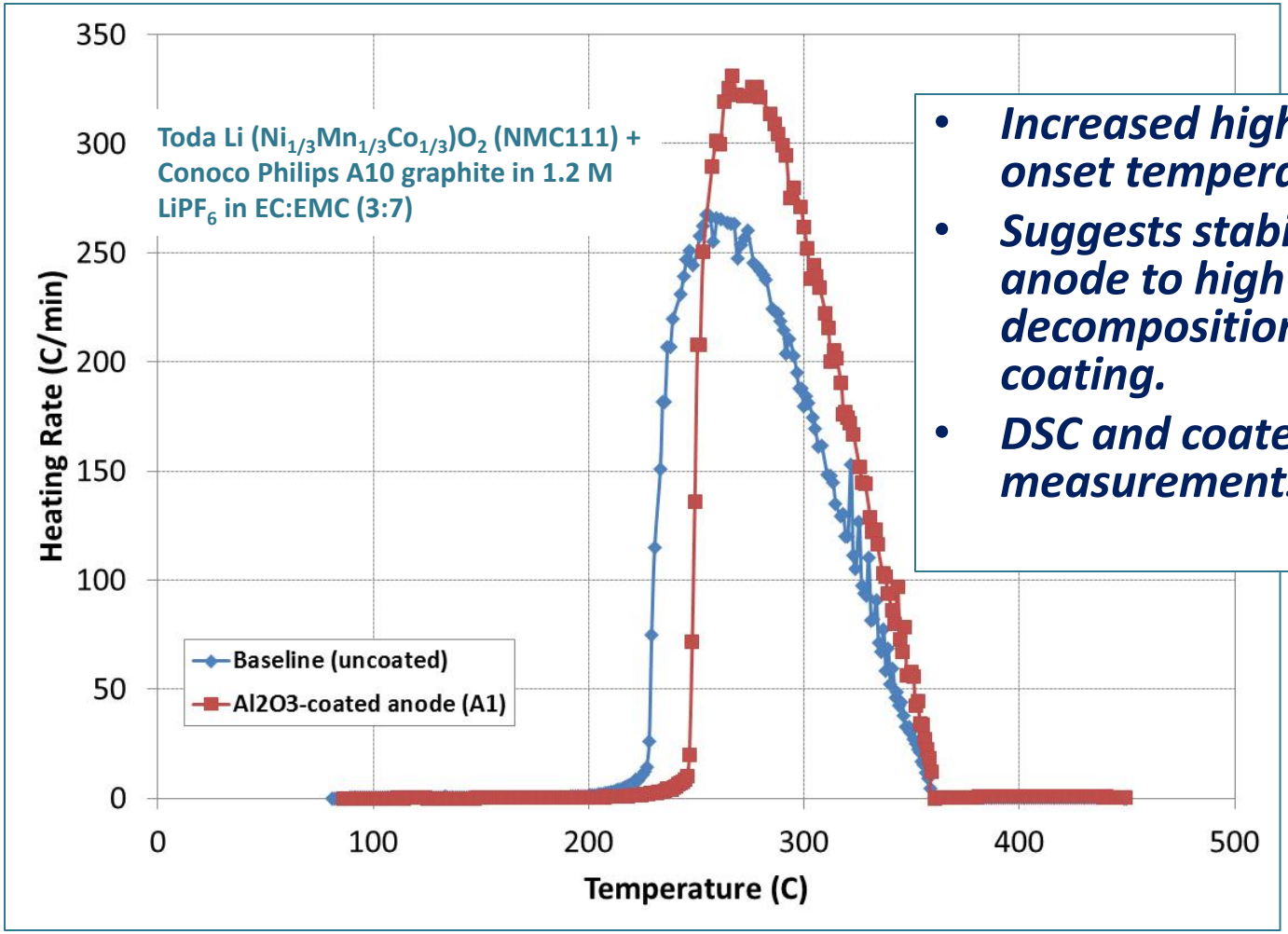
Use of rotary reactor appears to lead to increased cell failures, highlighting need for improved design.

18650 cells fabricated and tested at Sandia.



Initial data collected for larger format cells with commercially viable materials

Technical Accomplishments and Progress: Al_2O_3-Coated Commercial Electrodes (ALD)



- ***Increased high rate runaway onset temperature by 20˚C.***
- ***Suggests stabilization of the anode to high temperature decomposition by Al_2O_3 coating.***
- ***DSC and coated-cathode measurements in progress.***

First demonstration of improved performance with ALD coatings of commercially viable materials at 18650 cell size

Technical Accomplishments and Progress: Commercial Samples from ANL Cell Fabrication Facility

Standard materials received from Argonne Cell Fabrication Facility are currently being coated and tested for performance

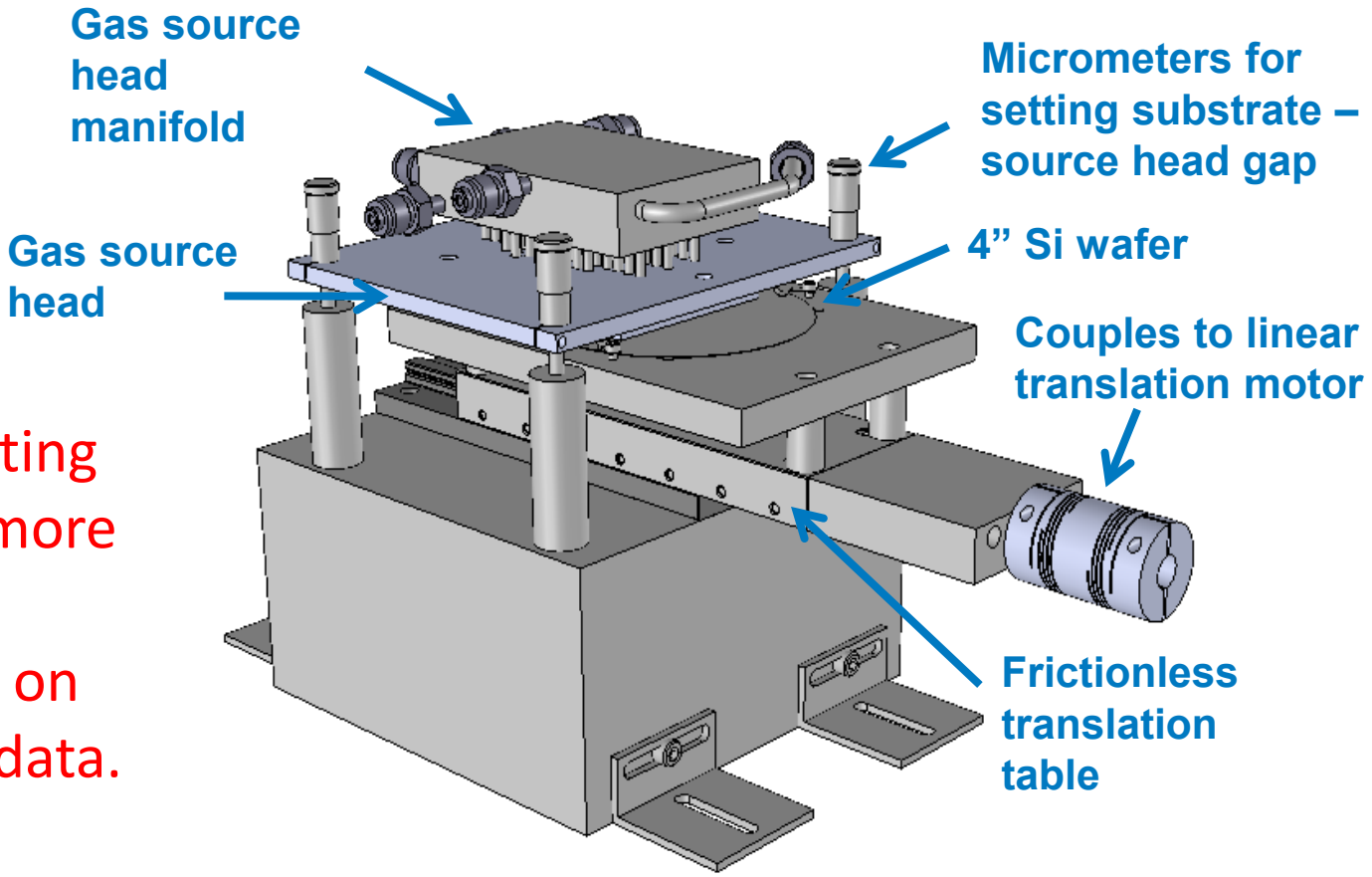
Formed Electrodes
A12 Graphite
Toda HE5050 NMC
Toda NCA
ANL Made LiNiMnO

Powders
ANL made LiNiMnO
Toda HE5050 NMC
A12 Graphite

Preliminary coin cell level testing of additional materials to determine best candidate system for scaling demonstrations.

Technical Accomplishments and Progress: Early Prototype Deposition System

Early prototype system is being leveraged to determine crucial design requirements for battery electrode coatings

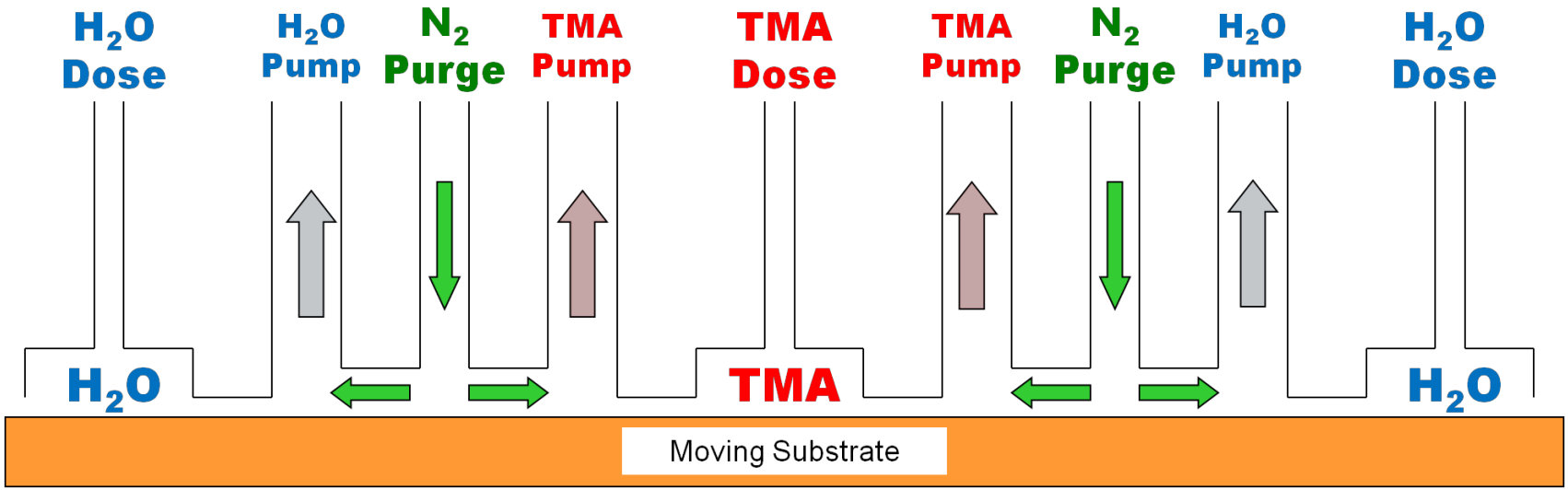


Leveraging existing system allows more rapid design progress based on actual process data.

P. R.Fitzpatrick, Z.M. Gibbs, and S.M. George, J. Vac. Sci. Technol. A **30**, 01A136 (2012)

Technical Accomplishments: AP-ALD Deposition Head Details

Two Al_2O_3 ALD cycles for every back-and-forth translation

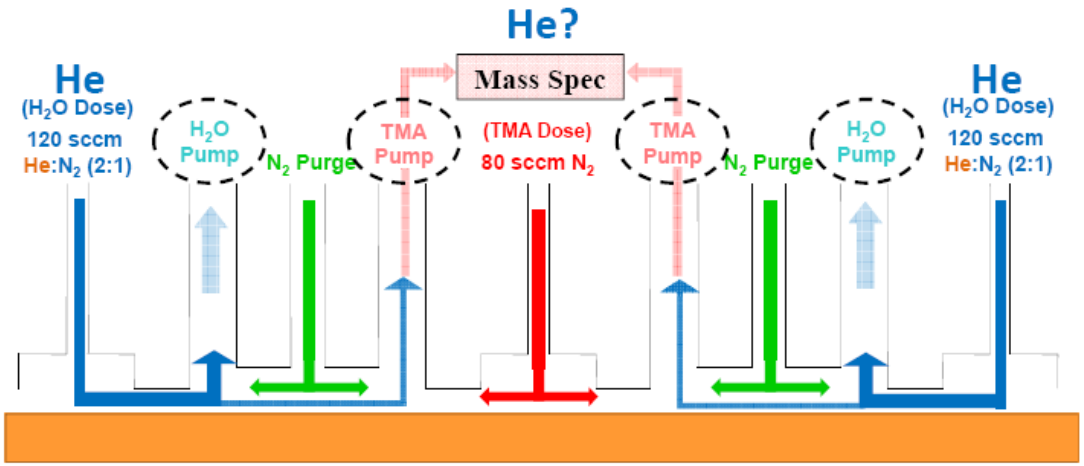


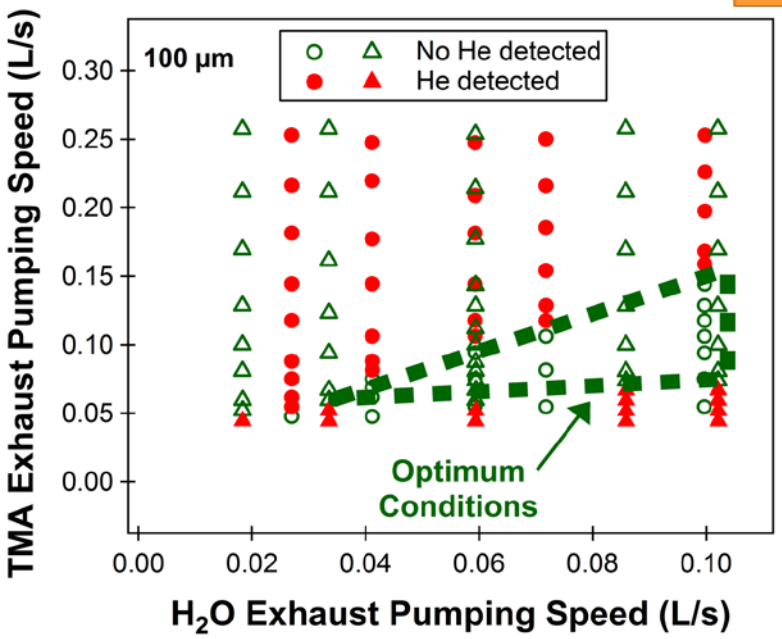
Similar design to gas source with purge and exhaust described in D.H. Levy et al., *J. Display Technol.* ***5, 484 (2009).***

Prototype system allows study of the effect of gap spacing; substrate speed; gas flow rates; exhaust channel pumping speeds; and pressure difference between reactant, purge, and curtain channels.

Technical Accomplishments and Progress

Helium detection used to determine optimal flow parameters to eliminate exposure of reactants prior to surface delivery

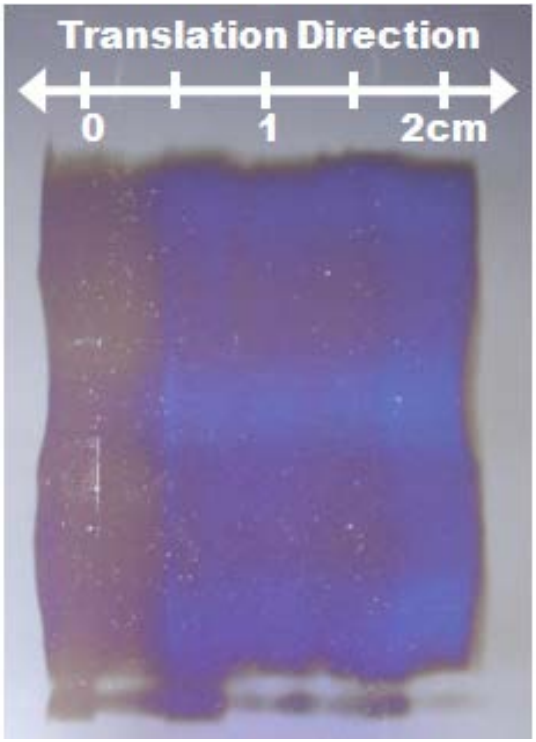




Outlined area shows region of optimal gas delivery and pumping conditions to allow in-line AP-ALD exposure

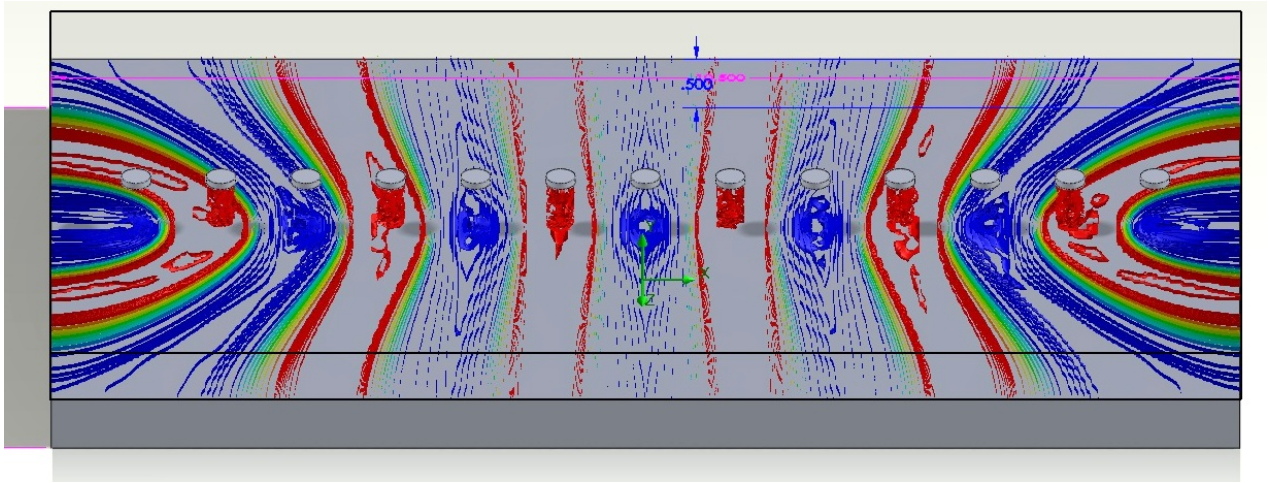
P. R.Fitzpatrick, Z.M. Gibbs, and S.M. George, J. Vac. Sci. Technol. A **30**, 01A136 (2012)

Technical Accomplishments: Deposition Optimization



Optimal conditions used to deposit alumina on silicon using prototype system

Non-uniformity indicates need for further refinement.



Computational Fluid Dynamics (CFD) calculations being employed to analyze improved reactor head designs

Collaborations and Coordination

- **University of Colorado at Boulder (Academic):**
  - Computational fluid dynamics simulation and deposition system design.
- **Sandia National Laboratories (Federal):**
  - Cell fabrication
  - Thermal and abuse tolerance testing
- **Argonne National Laboratory (Federal):**
  - Standard materials supply
  - Cell Fabrication

Proposed Future Work

- Demonstration of in-line AP-ALD coating for candidate systems based on performance in coin cell evaluations.
- Characterization of deposition on moving substrates to assess ability to integrate with manufacturing.
- Demonstration of device improvement at pouch cell level.
- Transfer of manufacturing viable coating process to industrial partners.

Summary

- All milestones are in progress and on schedule.
- Improved performance of 18650 cells with coated anodes have been demonstrated.
- Additional cells with coated cathodes are currently under test.
- Preliminary design of in-line AP-ALD deposition system has been demonstrated.
- Multiple electrode systems under evaluation for process scale up.
- Computational fluid dynamic simulations in place to refine preliminary design.

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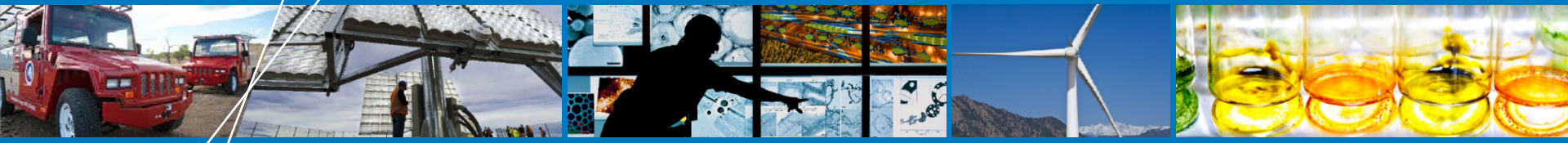
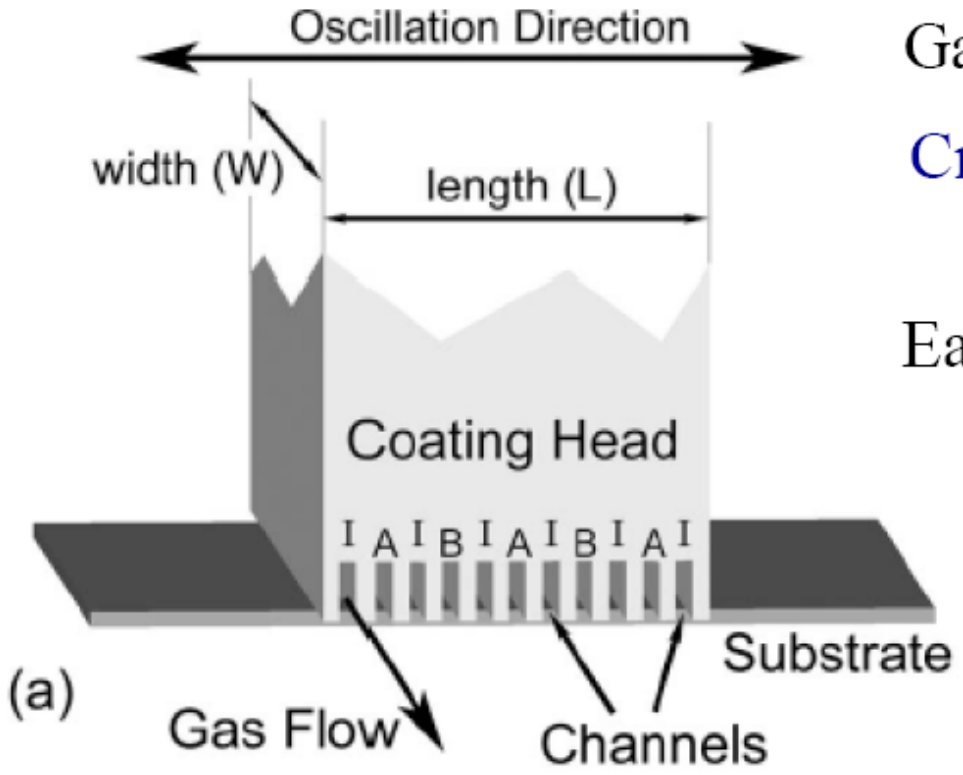


Technical Back-Up Slides

Relevance - Spatial ALD: Previous Demonstrations



Gap spacing of ~30 μm

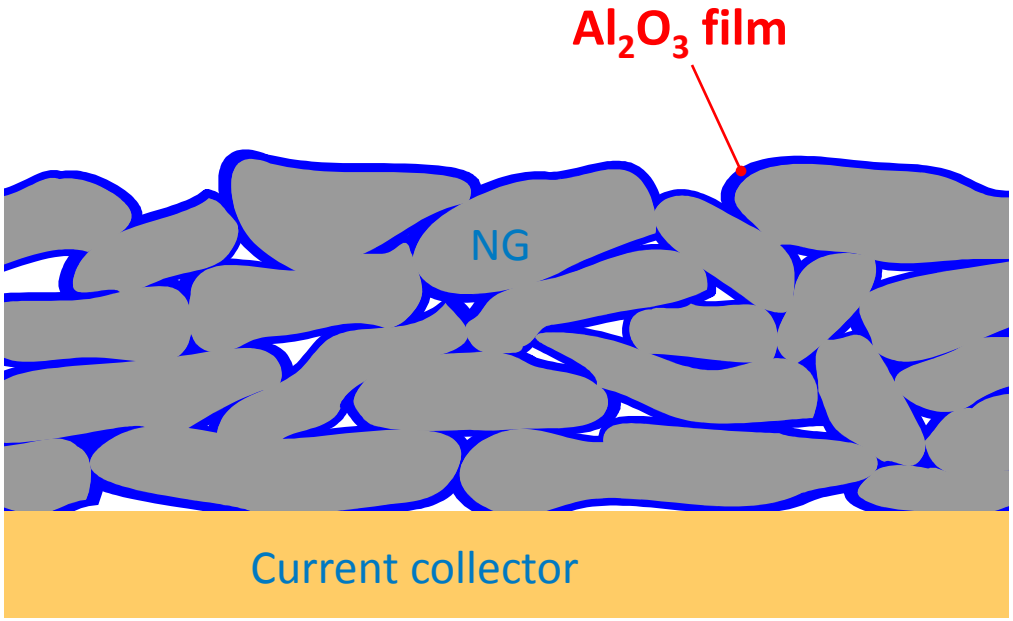
Cross flow of reactants & inert purge gas

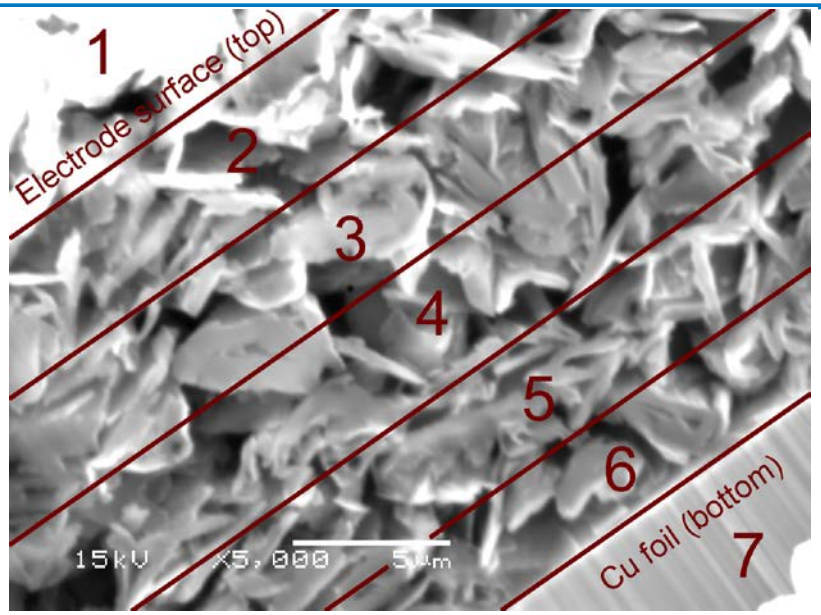
Each channel ~1 mm in width

AP-ALD is similar to large area coating systems capable of commercially viable processes that will meet battery manufacturing needs.

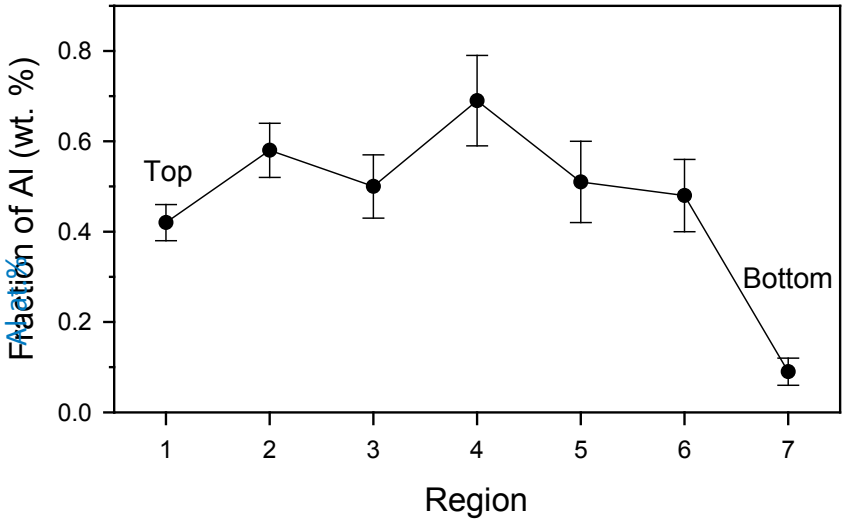
D.H. Levy et al., Appl. Phys. Lett. 92, 192101 (2008)

Direct ALD on As-Formed Composite Electrode



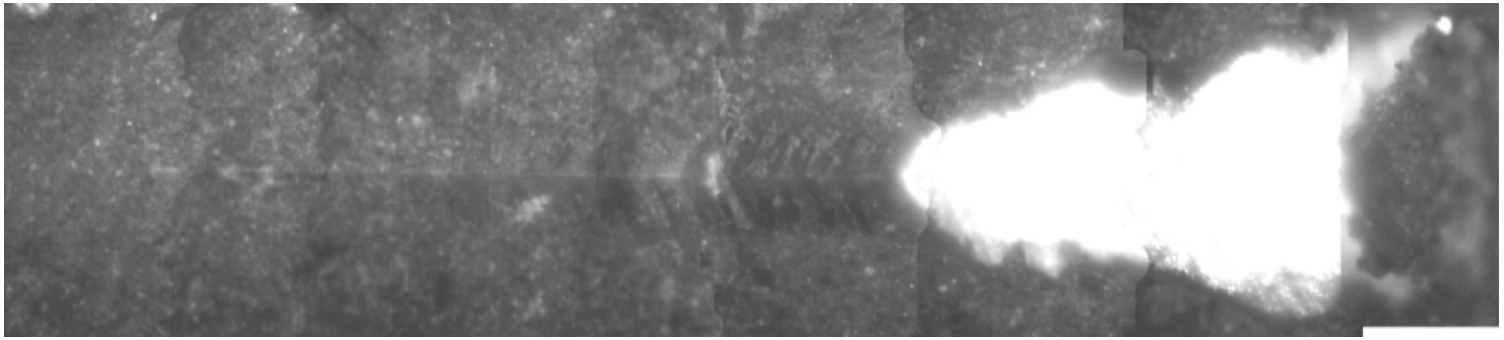


ALD Al_2O_3 appears to nucleate well on entire electrode surface but still allows electrical conductivity to be maintained.

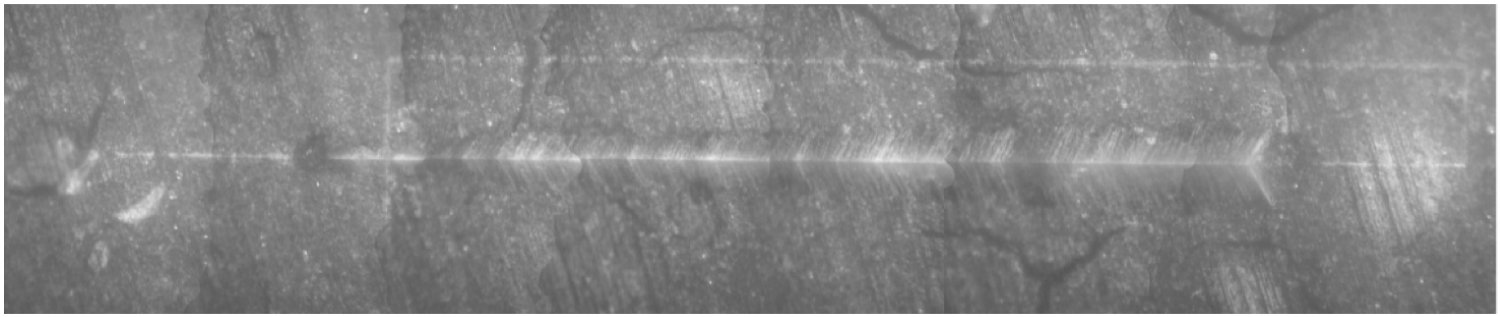


Scratch Test on Bare MoO_3 and Electrode Coated with ~ 8 Å Al_2O_3 via ALD

Bare Electrode



ALD Coated Electrode



80 mN of force applied across 600 µm results in complete exposure of the electrode (15 µm) before test completion confirming ALD coating provides strong adhesion to the electrode surface.

L.A. Riley, A.S. Cavanagh, S.M. George, S-H. Lee and A.C. Dillon, *Electochem. Solid State Letters* 14 (2011) A29.