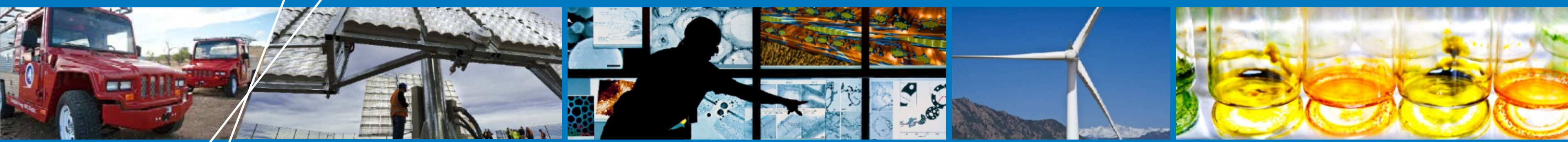
NREL
NATIONAL RENEWABLE ENERGY LABORATORY

2013 DOE Vehicle Technologies Program Review



ES#162: Development of Industrially Viable Electrode Coatings

Robert C. Tenent
National Renewable Energy Laboratory

Project Overview

Timeline

- Project Start Date: 12/2011
- Project End Date: 9/2013
- Percent Complete: ~80%

Barriers

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

Budget

- Total Project Funding: $450K
- DOE Share: $450K
- Contractor Share: N/A
- FY12 Funding: $300K
- Funding for FY13: $150K
- FY14 Anticipated Funding:
  AOP $0K; FOA $400K

Partners

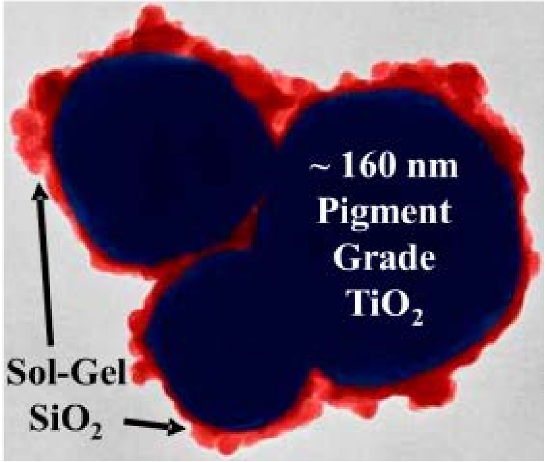
- NREL (Lead)
- University of Colorado – Boulder
- Sandia National Laboratory
- Argonne National Laboratory
- Oak Ridge National Laboratory

Relevance and Objective

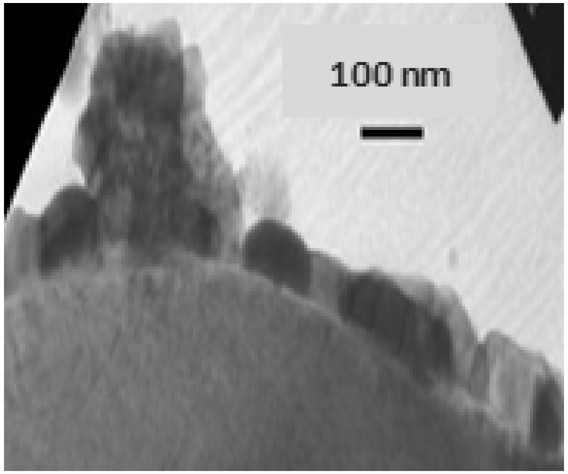
- The ABR program is focused on improving cycle life, abuse tolerance and reducing cost for PHEV battery technologies.
- Previous work conducted by NREL and the University of Colorado at Boulder has demonstrated that thin, conformal coatings of lithium ion battery electrodes formed by atomic layer deposition (ALD) can dramatically improve abuse tolerance and cycle life which in turn reduces ultimate cost.
- Current technology for performing ALD is not amenable to high throughput manufacturing methods and thus represents a high priced bottleneck in the implementation of ultrathin electrode coatings at a commercial scale.
- ***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.

Approach - Comparison of Common Coating Technologies

Sol-Gel

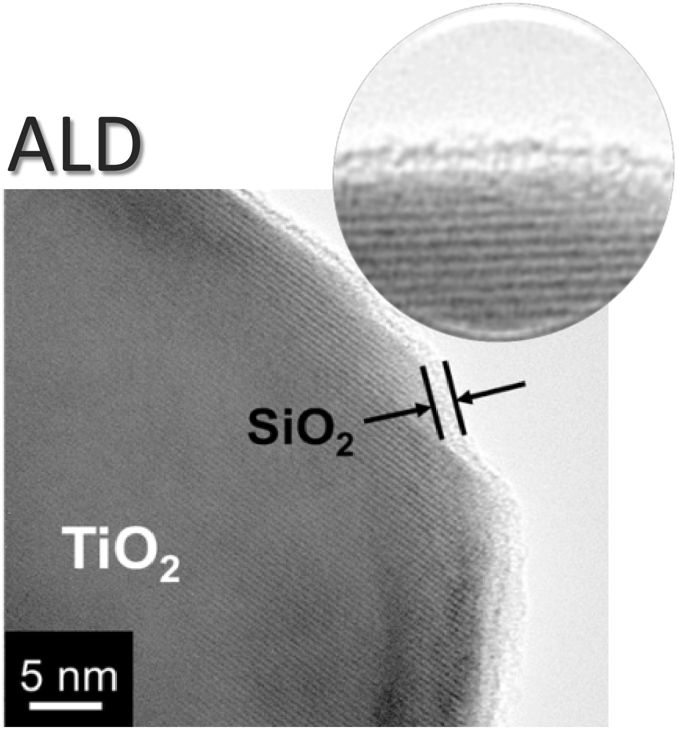


CVD



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

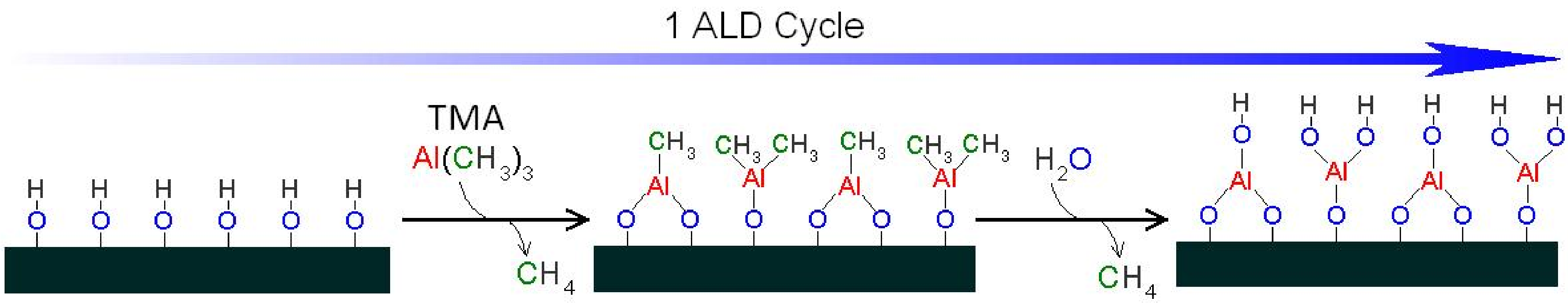
ALD



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:

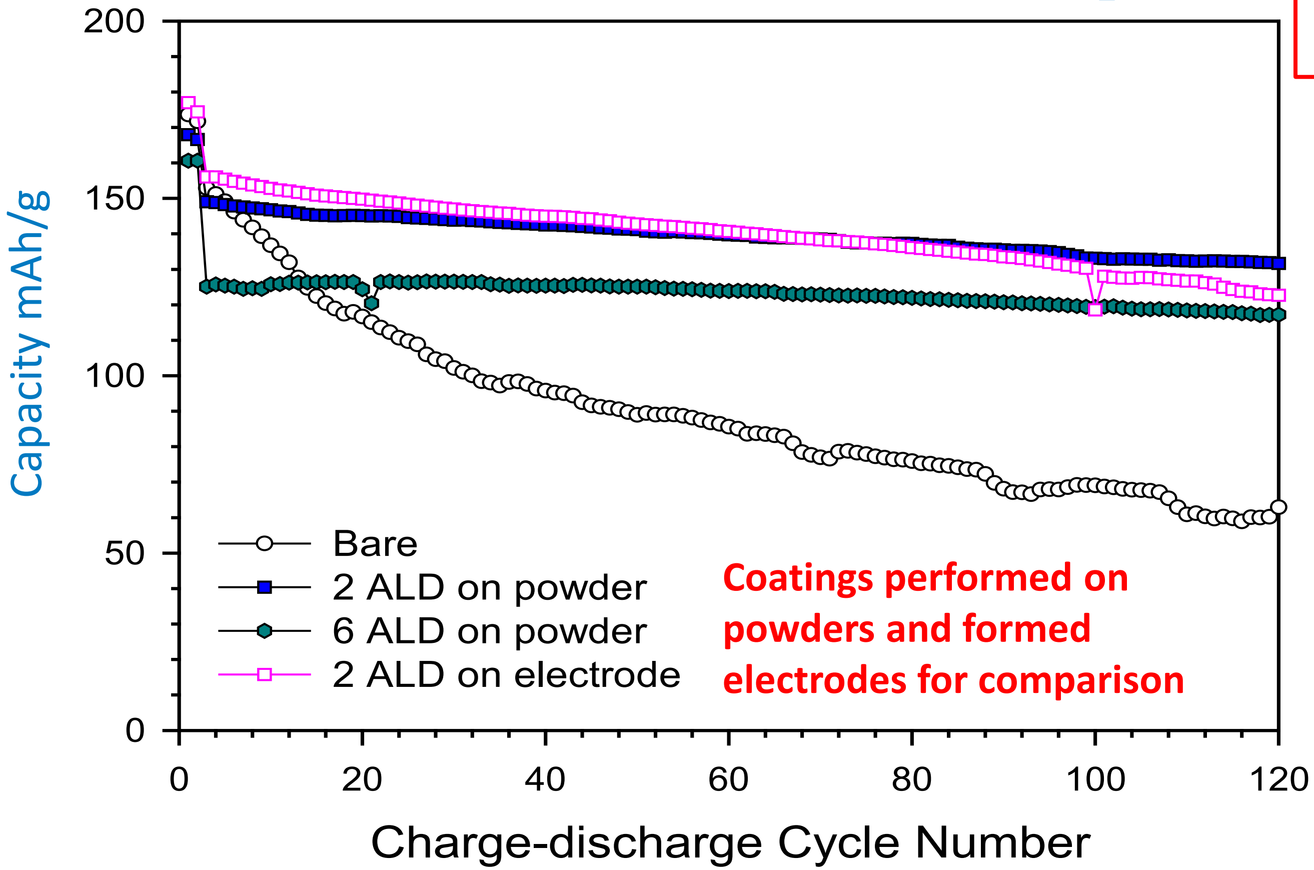


- **Conformal**
- **Monolayer thickness control (~1 Å)**
- **Especially powerful for nano-structured materials**
- **Commercially scalable (No solvent**, no excessive amount of precursors, No post-heat-treatment at high-temperature)
- **Here we will enable integration of "ALD-like" processes into existing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



Please see Project ES 145 for further developmental coatings work

1 C-rate (140 mA g^{-1})
3.3-4.5 V **(*vs.* Li/Li^+)**

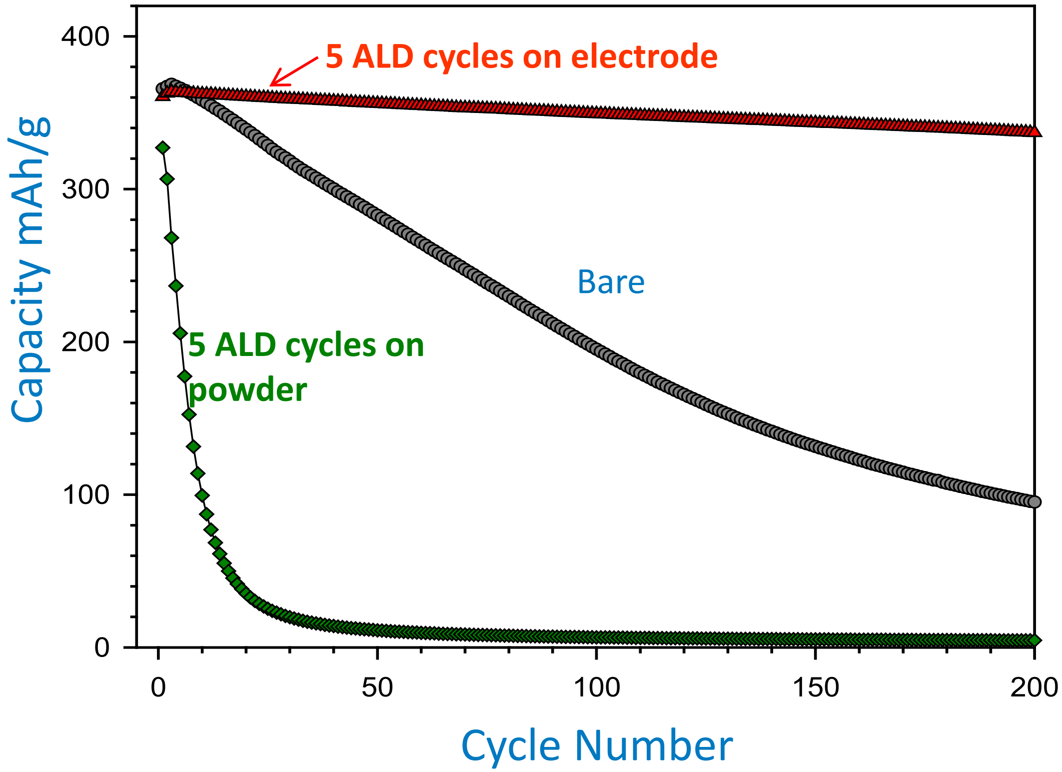
ALD coating appears to limit degradation of $LiCoO_2$ at high potential.

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



Please see Project ES 145 for further developmental coatings work

Cycling at High Temperature Generally Leads to Rapid Capacity Fade.

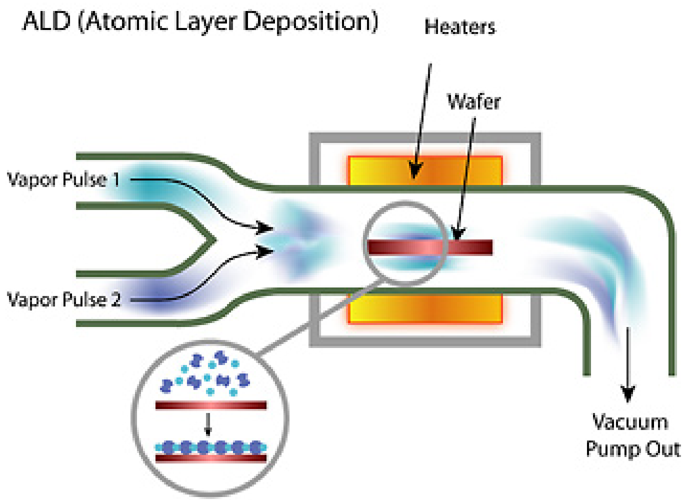
ALD coatings may allow stable performance at increased temperature

ALD coatings of formed electrodes gives improved performance over coated powders

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.

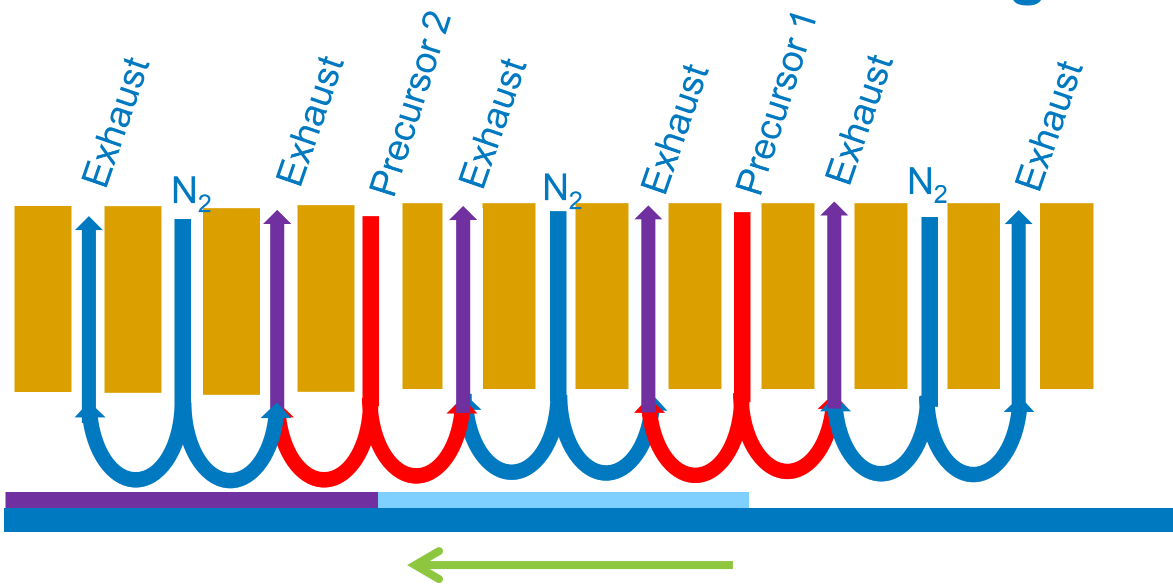
Approach: Atmospheric Processing-ALD (AP-ALD) for Battery Industrial Fabrication Lines

Present ALD Capabilities



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

In-line AP-ALD for Manufacturing



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

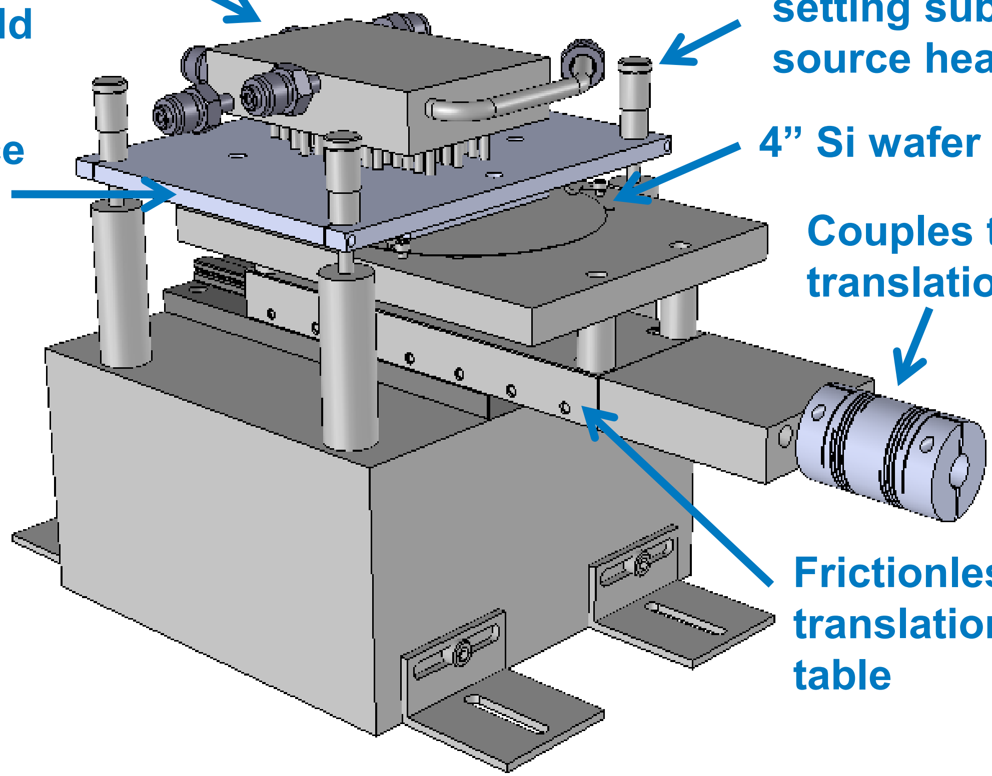
Similar to known CVD based high throughput manufacturing processes

Milestones

Date Due	Milestone	Status
May 2012	Demonstration of an Al_2O_3 ALD coating showing improved performance for a commercially viable cathode material	Complete
September 2012	Establish a deposition system capable of in-line (AP-ALD) on at least 6 in. by 6 in. up to 12 in. by 12 in.	Complete
On-going	Continued supply of ABR collaborators with alumina ALD coated electrodes and materials	On-going
September 2013	Design and construction of prototype in-line ALD coater for deposition on porous substrates	On-Schedule

Technical Accomplishments: Demonstration of In-Line AP-ALD

An early prototype system was developed to assess the viability of conducting in-line ALD under atmospheric pressure conditions

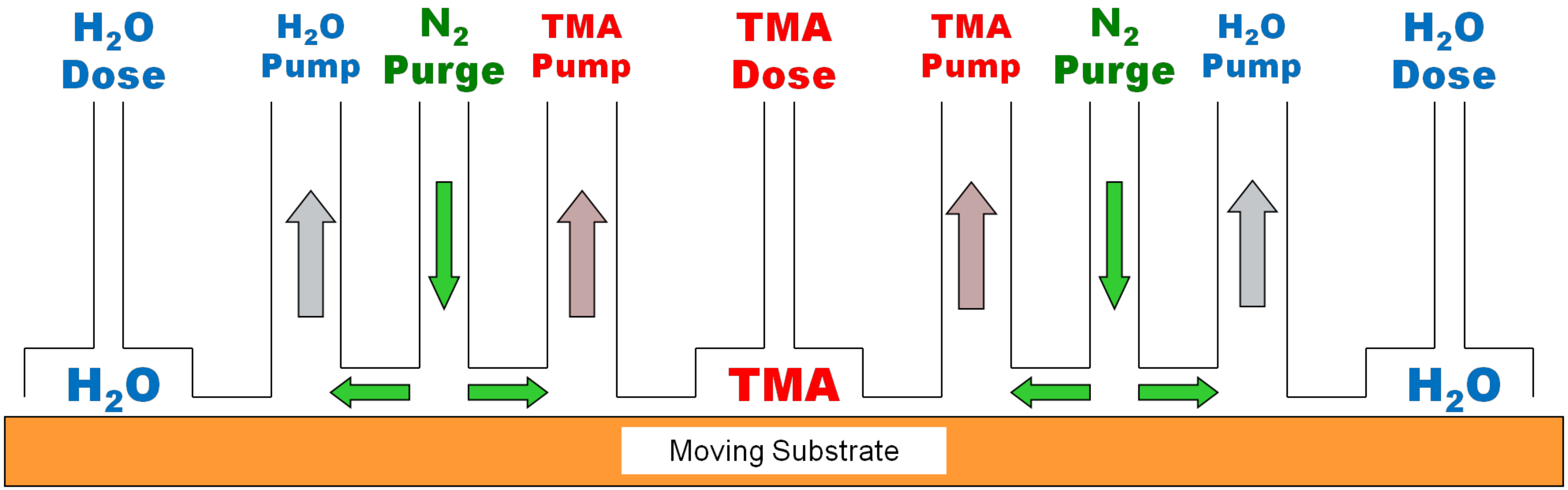


Early demonstration experiments were performed on 4” silicon wafers

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

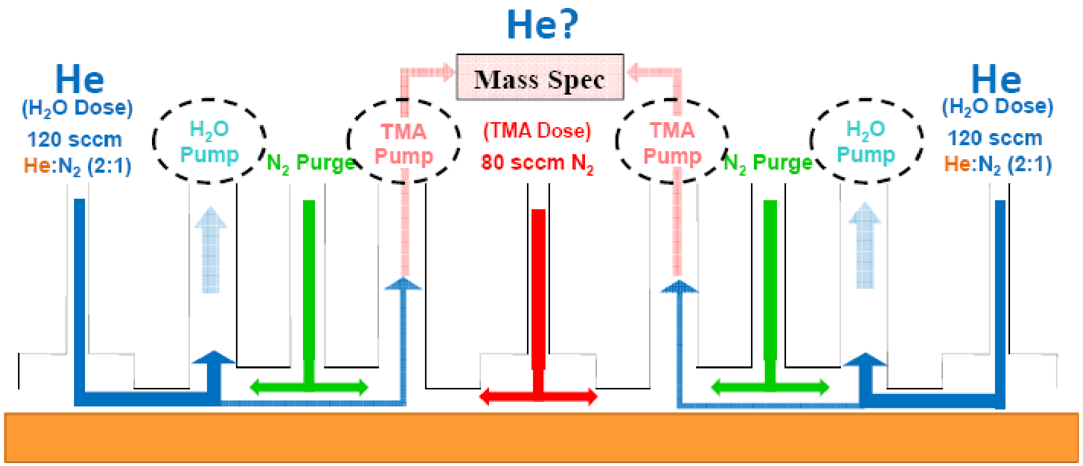


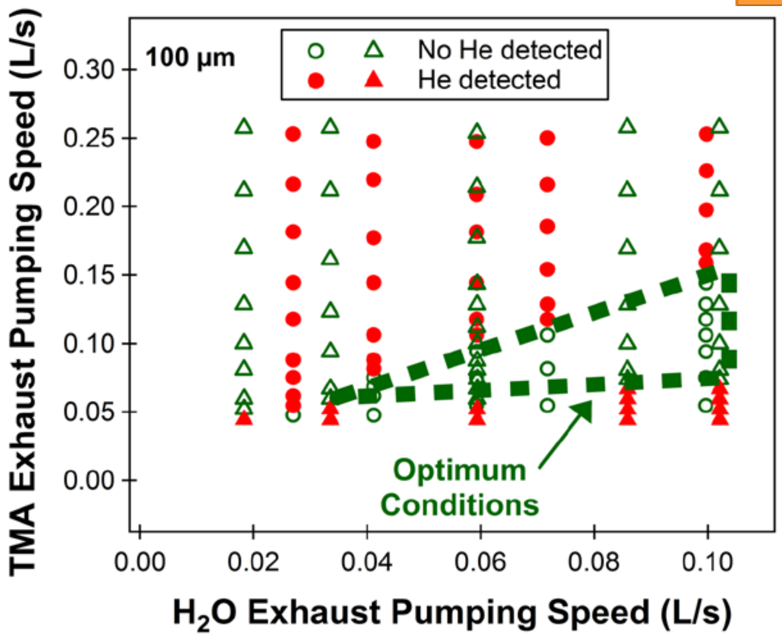
Similar design to gas source with purge and exhaust described in
D.H. Levy et al., *J. Display Technol.* ***5, 484 (2009).***

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



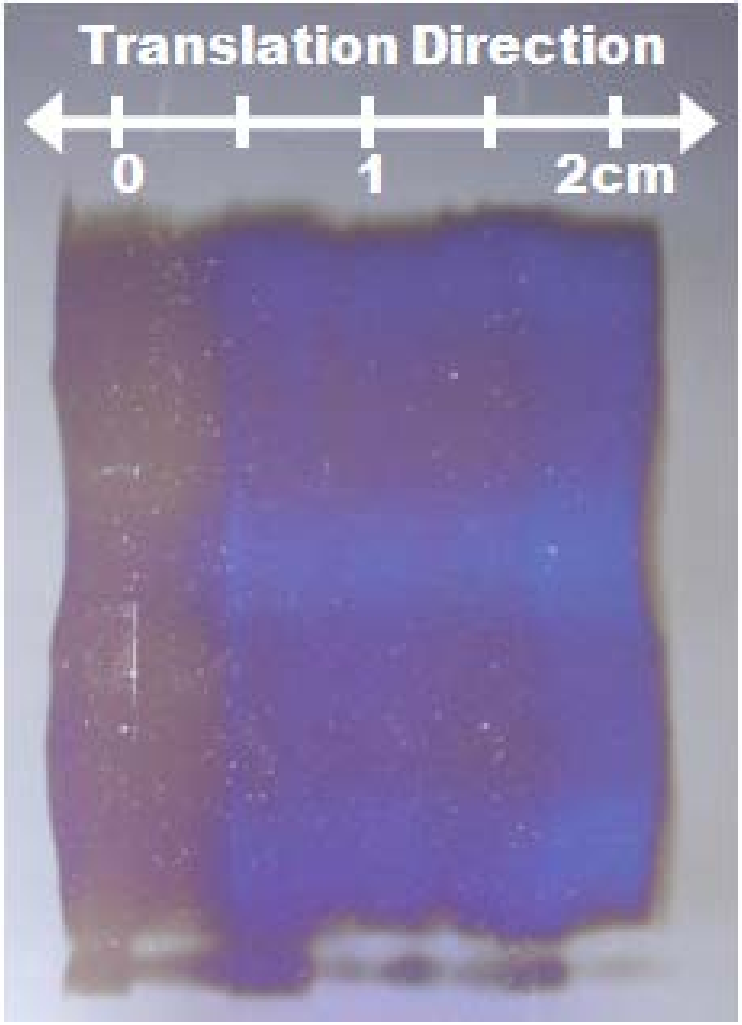


Outlined area shows region of optimal gas delivery and pumping conditions to allow in-line AP-ALD exposure

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

Technical Progress and Accomplishments:
Early Demonstration of In-Line ALD on Flat Substrates

Alumina film deposited via in-line AP-ALD



Optimal conditions from earlier analysis were employed to deposit alumina on silicon using prototype in-line deposition system

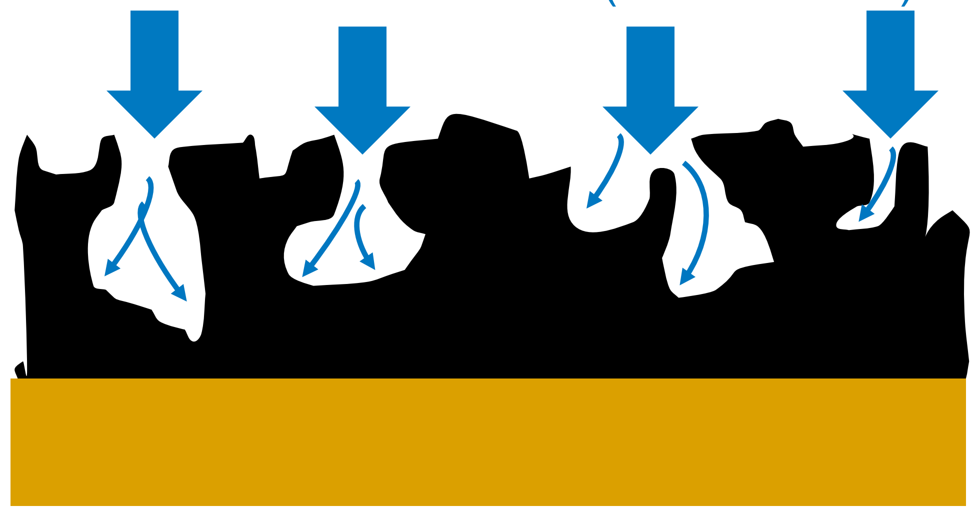
Non-uniformity possibly indicates zones of precursor mixing and CVD like deposition

While preliminary deposition equipment has been used to perform in-line demonstrations, a new design is required that takes into account the specific needs of a battery manufacturing process.

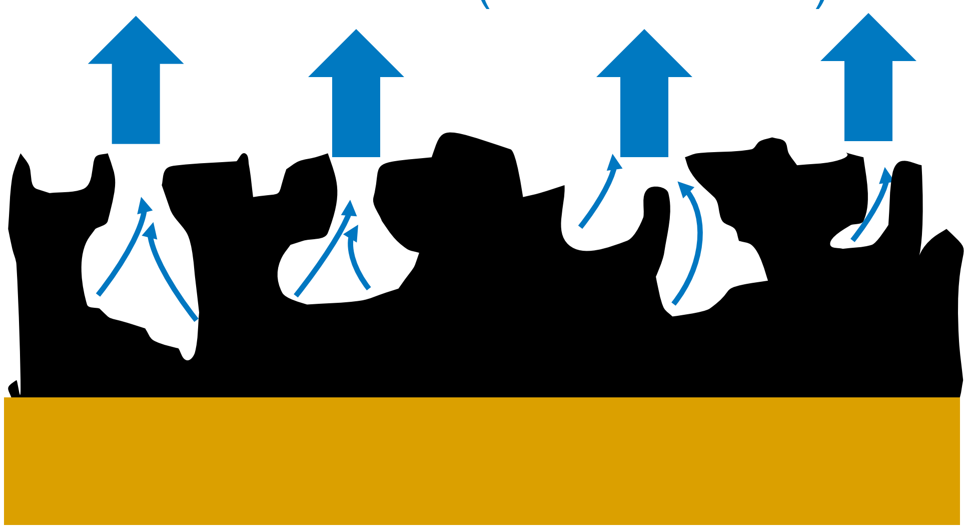
Approach: Another consideration…porosity

Effective ALD coating of a porous battery electrode requires that gas phase precursors be able to fully penetrate the electrode as well as be removed in a time effective manner.

Precursor Penetration and Saturation
mTorr of ALD Precursor (Viscous Flow)

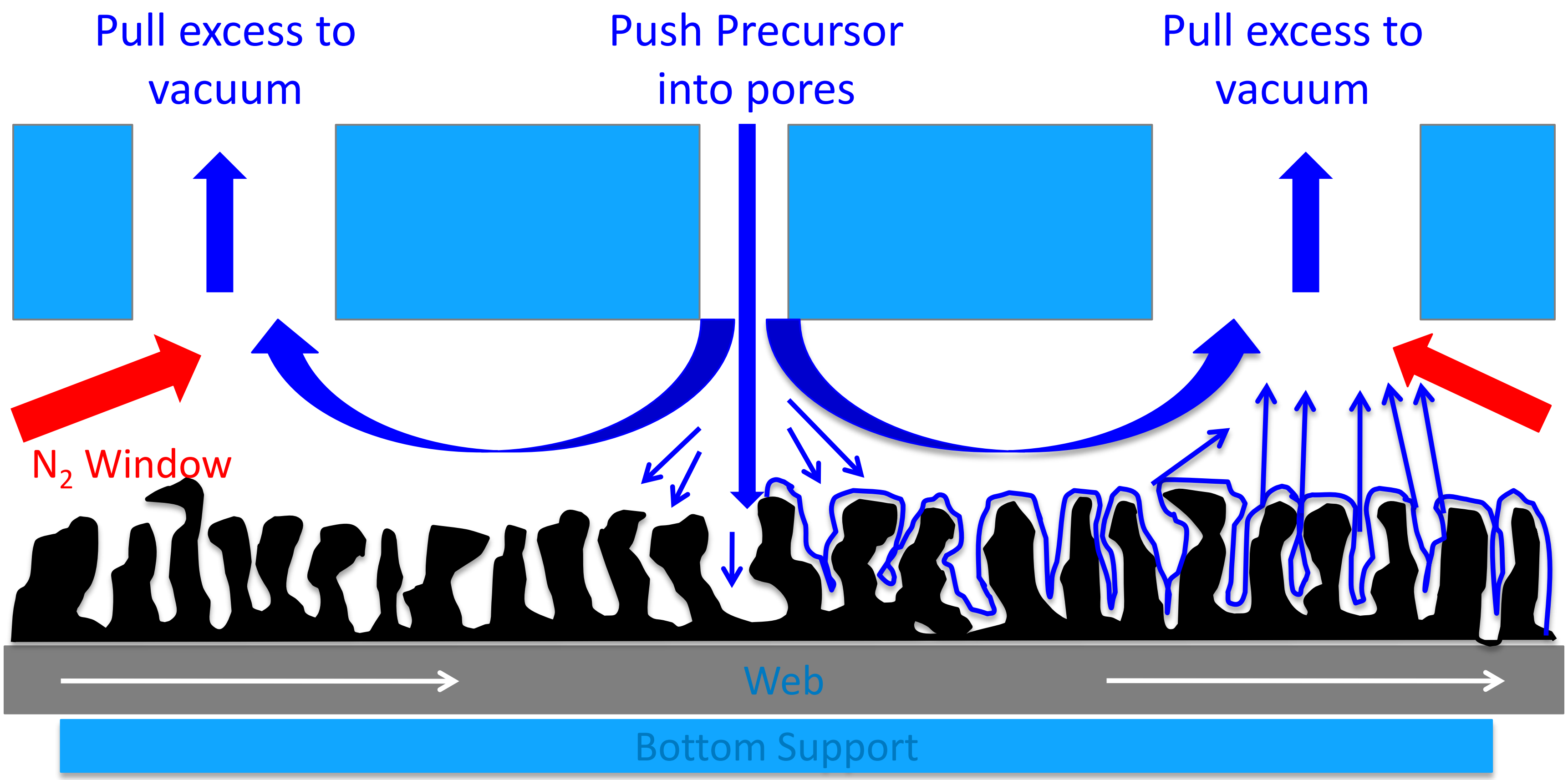


Residual Precursor Removal
Low Pressure (Molecular Flow)



This requires disparate pressure zones be employed with moderately high pressures (100mTorr) used to drive precursor into the film and low pressures used for rapid precursor removal.

Approach: “Push-Pull” In-Line ALD

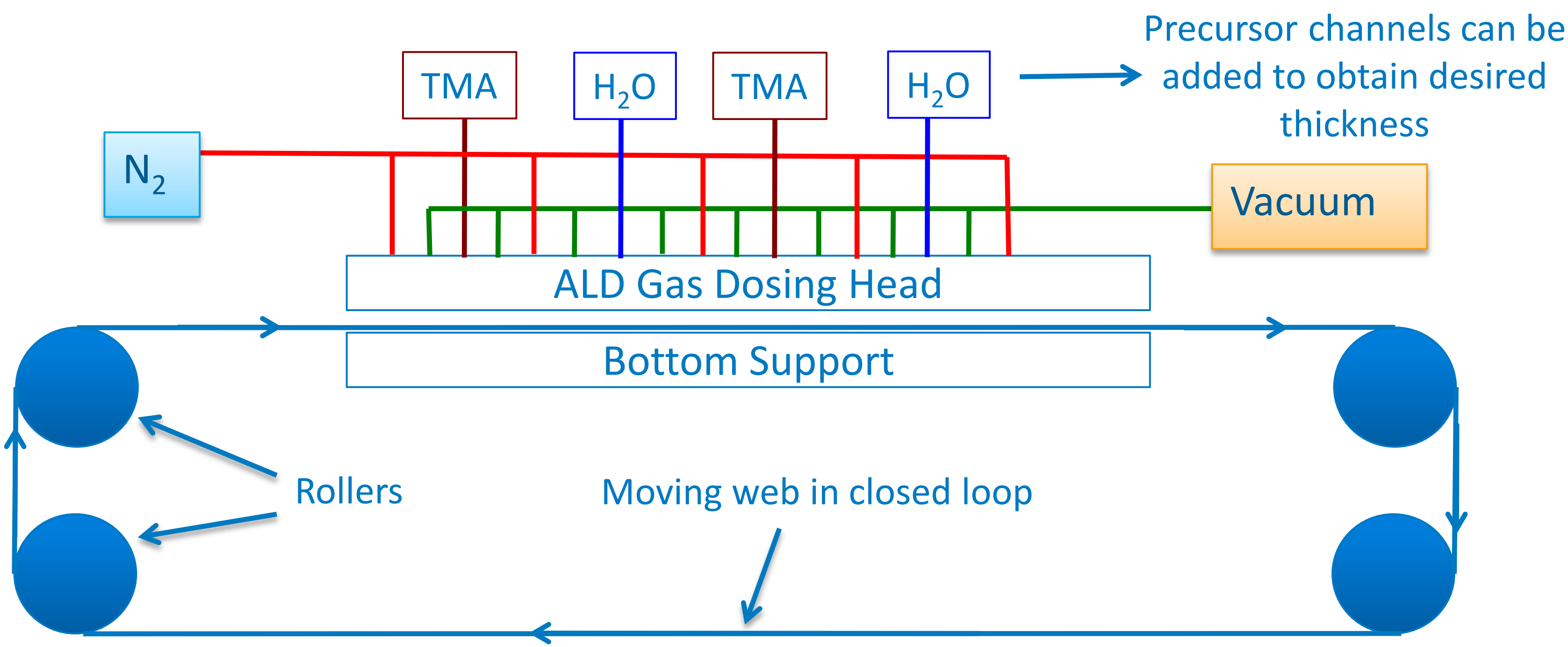


“Push-Pull” design for Roll to Roll In-Line ALD in porous battery materials

- High pressure reactant pushed into pores
- Excess reactant and reaction product pulled out by vacuum region
- N_2 used to separate reactants and provide entrainment

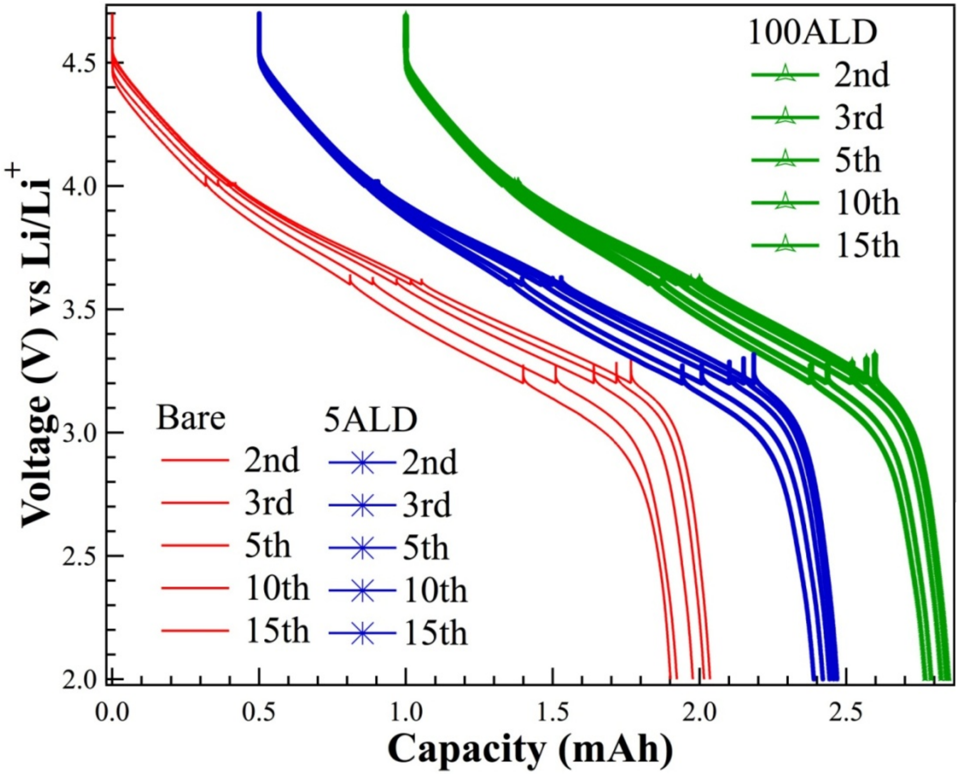
Technical Progress and Accomplishments: Improved design for roll to roll format ALD on porous substrates

Our next generation roll to roll "push-pull" reactor is being designed into a low profile format that will allow use with a circulating electrode slurry coated foil



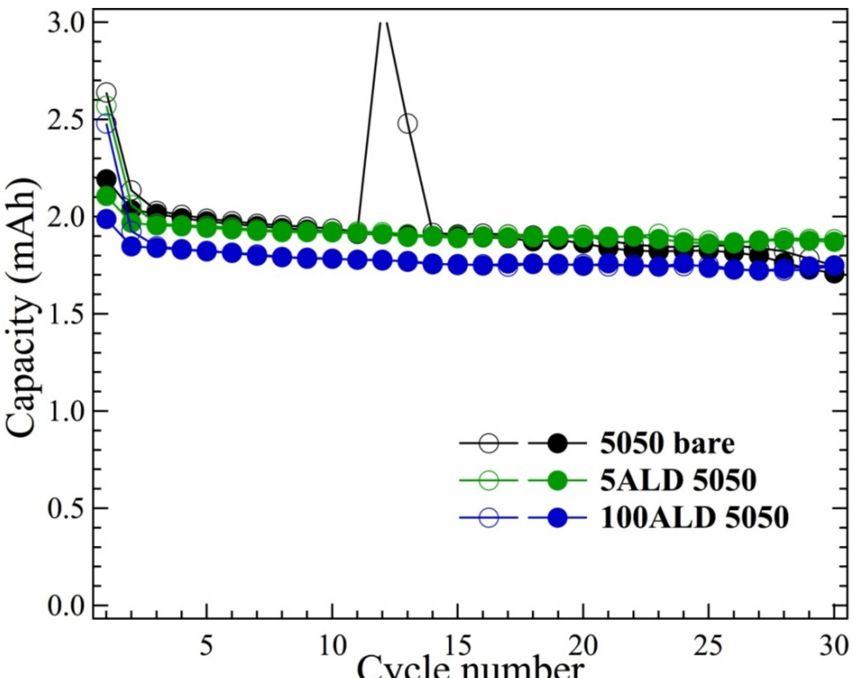
- Low profile format should ease integration into existing equipment.
- Calculations are currently underway to determine optimum geometry for dosing head channels.
- Fabrication of initial dosing head will be begin shortly.

Technical Progress and Accomplishments: Coatings Support of ABR Collaborators



As part of our collaboratory efforts with Argonne NL, we have assisted in determining the effect of surface coating upon the performance of the HE5050 cathode material.

Electrodes as well as powders were coated with ALD alumina and tested.



Data is being jointly analyzed between the two laboratories at this time. Preliminary results appear to indicate that ALD coating may improve cycling durability, however, has limited impact on the voltage fade phenomenon observed for this material.

Technical Progress and Accomplishments: Support of Additional ABR Laboratories

Sandia National Laboratories

In collaboration with Sandia NL, NREL has coated both Toda NMC111 and Conoco Philips A10 Graphite electrodes and powders for use in assessing possible safety improvements due to ALD coatings.

NREL is currently working with Oak Ridge NL in order to determine effects of ALD coating on the ABR baseline NMC523 cathode material in preparation for future collaborations on scaling of in-line AP-ALD

Collaborations and Coordination

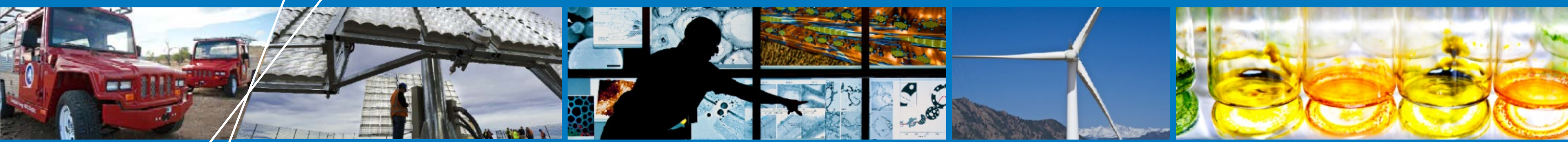
- **University of Colorado at Boulder (Academic):**
  - Computational fluid dynamics simulation and deposition system design.
- **Sandia National Laboratories (Federal):**
  - Cell fabrication
  - Thermal and abuse tolerance testing
- **Argonne National Laboratory (Federal):**
  - Evaluation of coating effect on voltage fade phenomenon
  - Supply of standard materials and cell fabrication
- **Oak Ridge National Laboratory (Federal):**
  - Planning for scaling to larger format roll to roll coatings

Proposed Future Work

- **Final construction and demonstration of baseline “push-pull” in-line reactor.**
- **Demonstration of “push-pull” generated coatings on slurry-coated electrode foils.**
- **Continued evaluation of performance of ALD coatings on high energy cell materials at coin and pouch cell levels.**
- **Planning to extend this work and use findings in a proposal to DOE VTP FOA in FY14.**

Summary

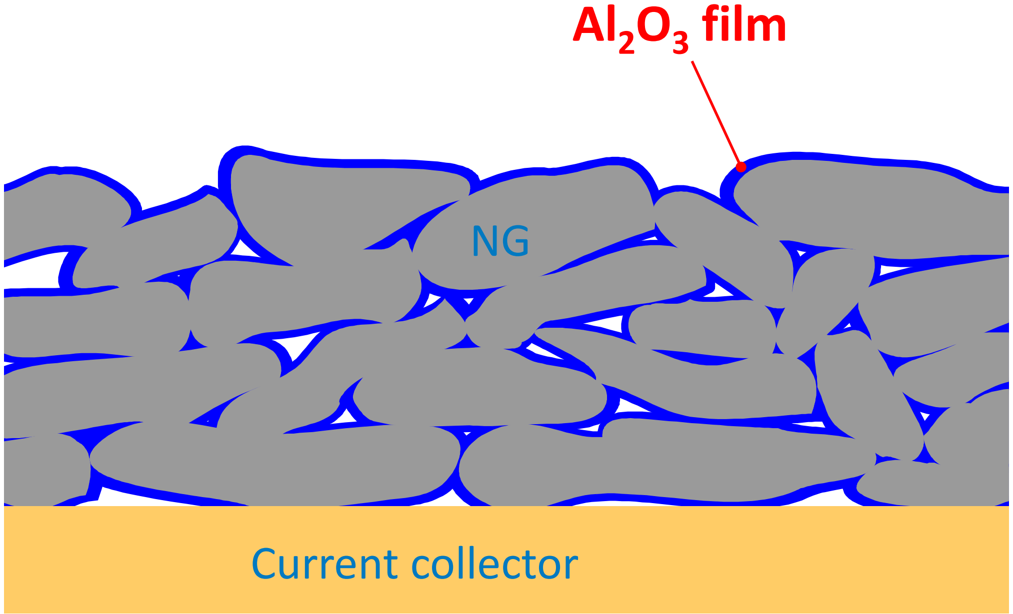
- All milestones have been completed on schedule or are currently in process.
- Atmospheric pressure ALD coatings have been proven feasible in an in-line format.
- An improved reactor design is in process to enable deposition on highly porous substrates.
- Multiple electrode materials have been evaluated for partner laboratories including studies of the voltage fade effect for the HE5050 material.
- NREL has developed internal capabilities for coatings on up to 6” by 6” electrode foils for pouch cell evaluation purposes.

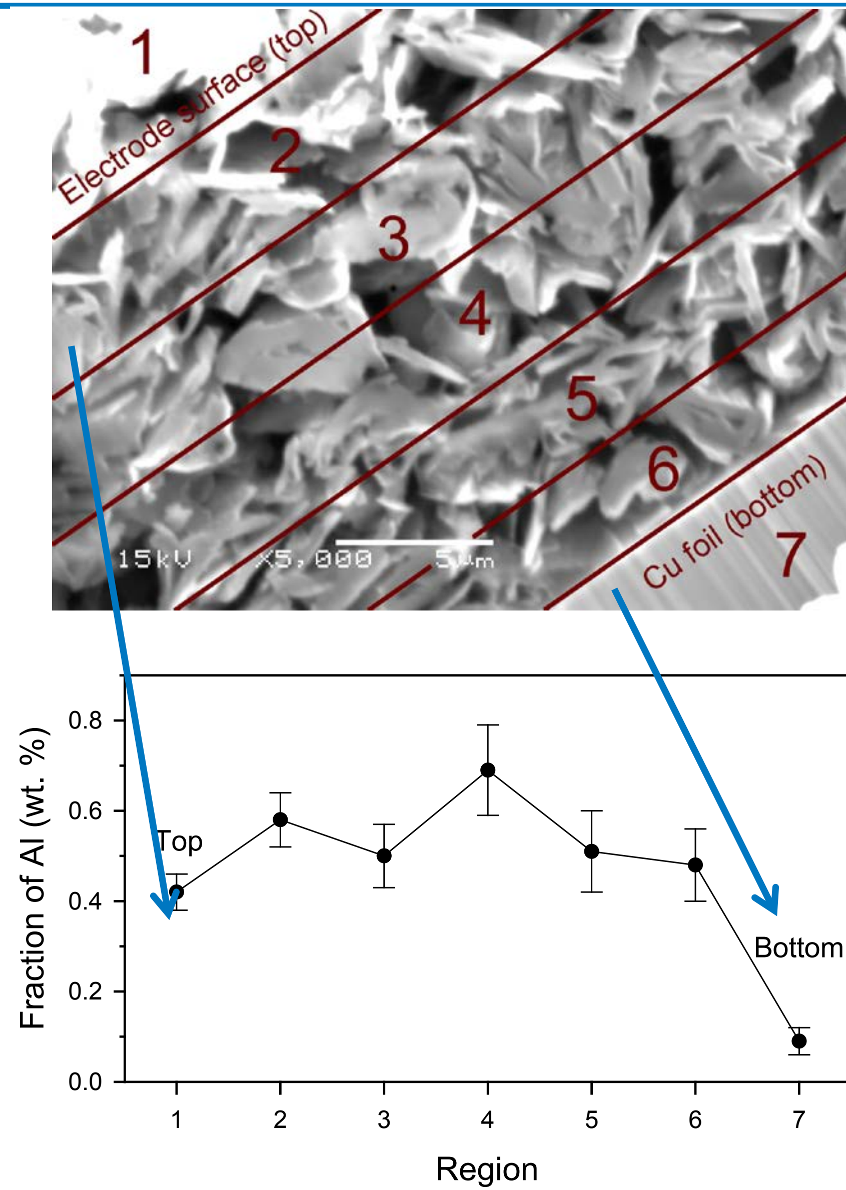


Technical Back-Up Slides

Direct ALD on As-Formed Composite Electrode

Cross sectional analysis indicates successful penetration and coating of a porous electrode





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

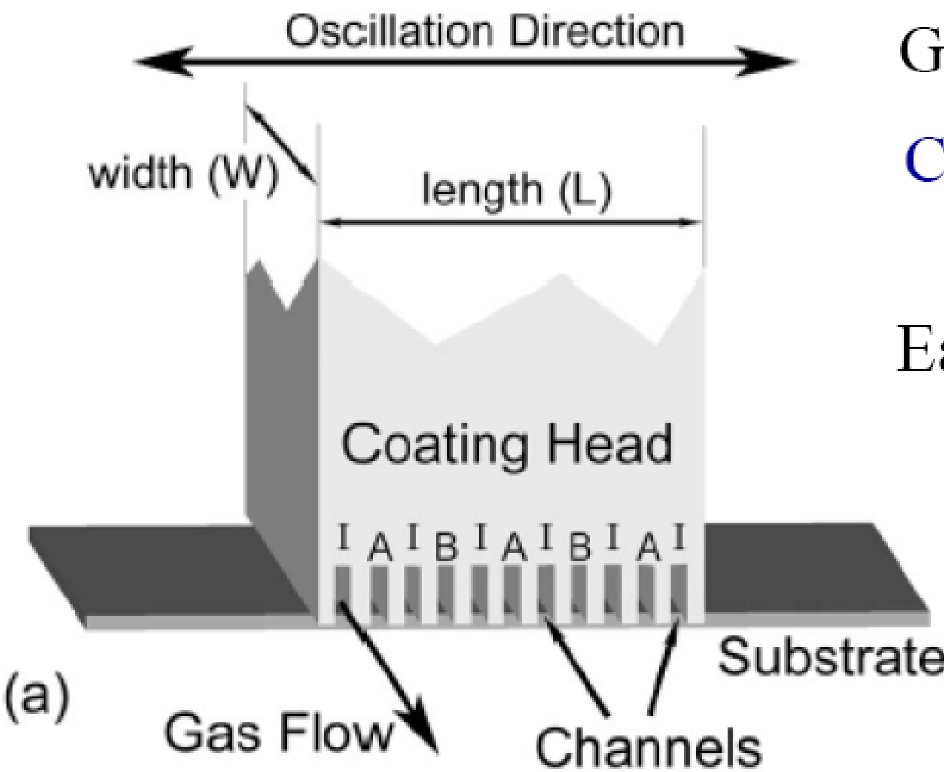
Coating of Larger Format Electrodes

Beneq large format ALD system

6” by 6” foil coated with Toda HE5050 and 20 cycles of ALD alumina

- Large format ALD methods have been employed to allow coating of larger format battery electrodes.
- Initial sample depositions just completed and sample analysis for uniformity of deposition and device performance is currently initiating.

Spatial ALD: Previous Demonstrations



Gap spacing of ~30 μm

Cross flow of reactants & inert purge gas

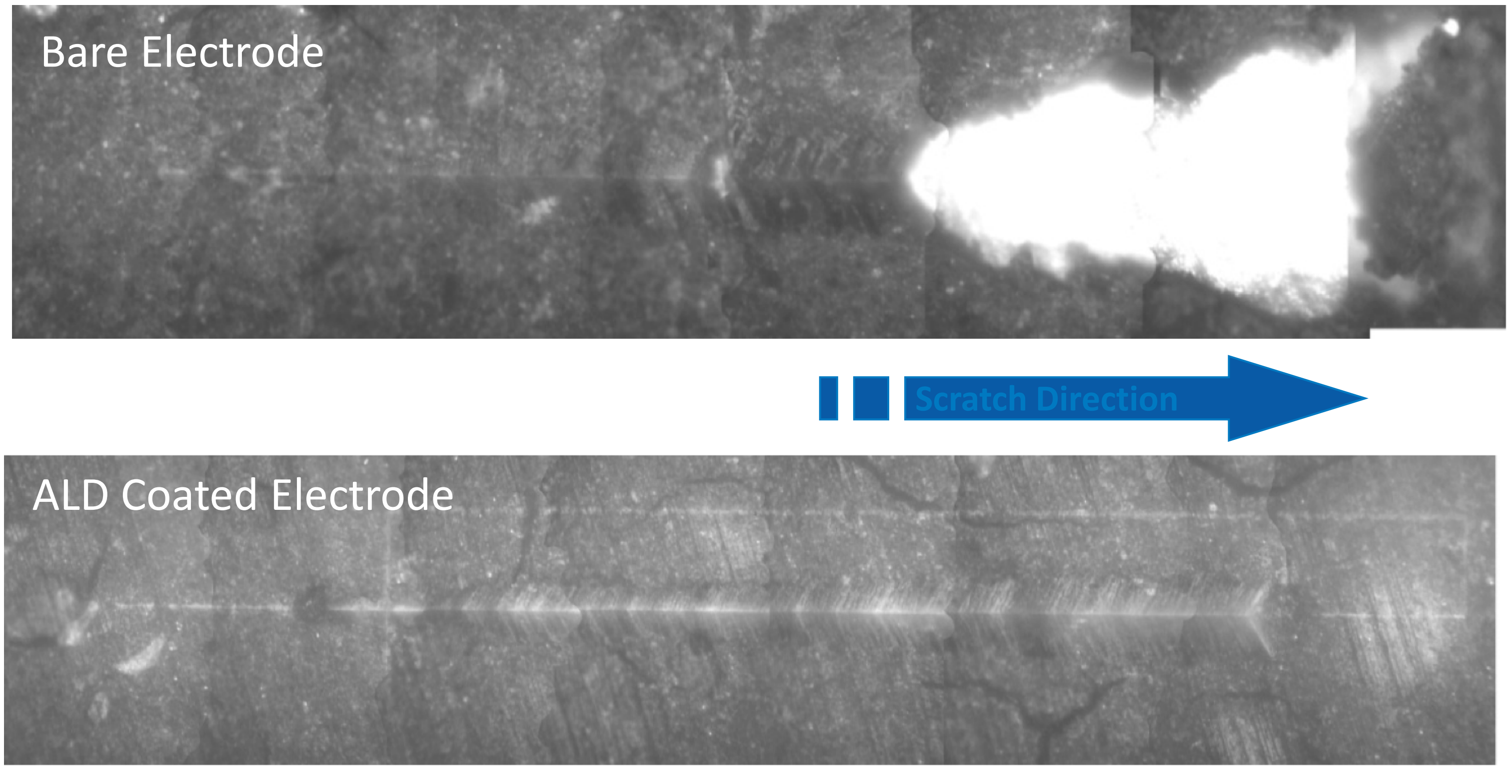
Each channel ~1 mm in width

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)

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

Mechanical property analysis appears to indicate that coatings impart more structural stability to formed electrodes

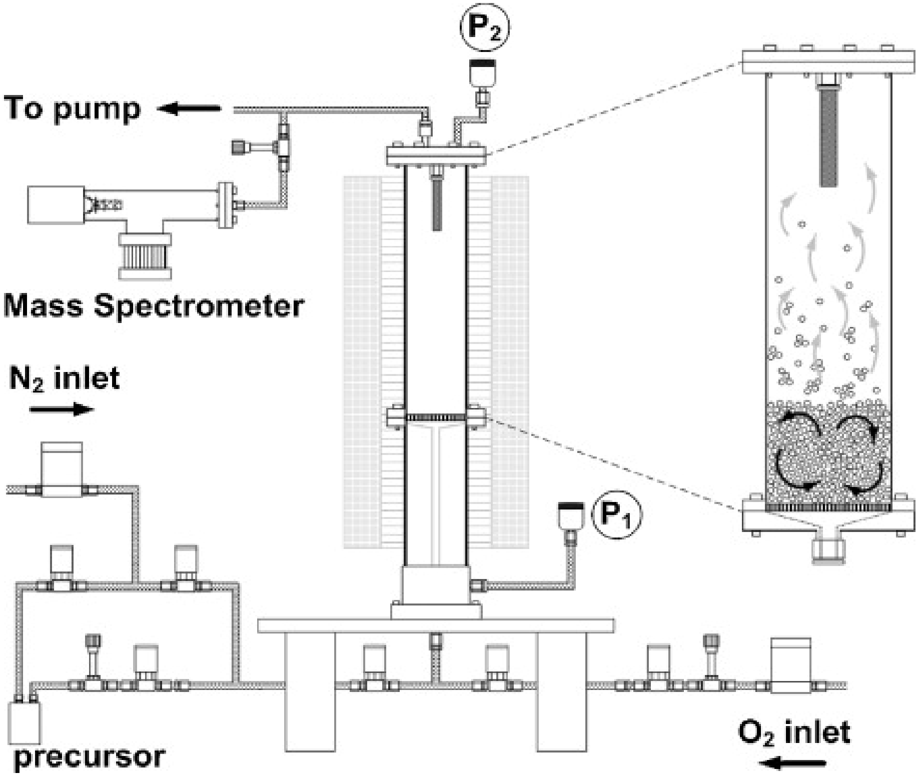


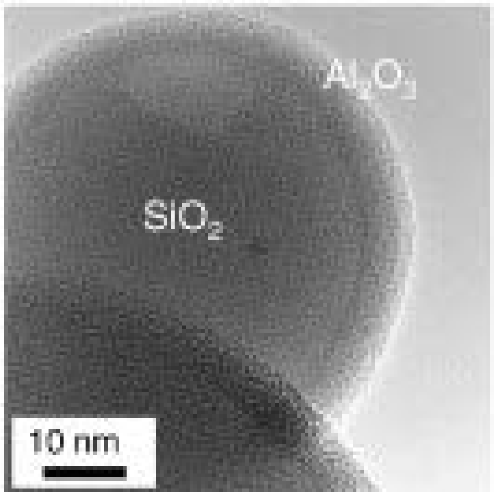
80 mN of force applied across 600 µm results in complete exposure of the electrode (15 µm) before test completion confirming ALD coating provides strong adhesion to the electrode surface.

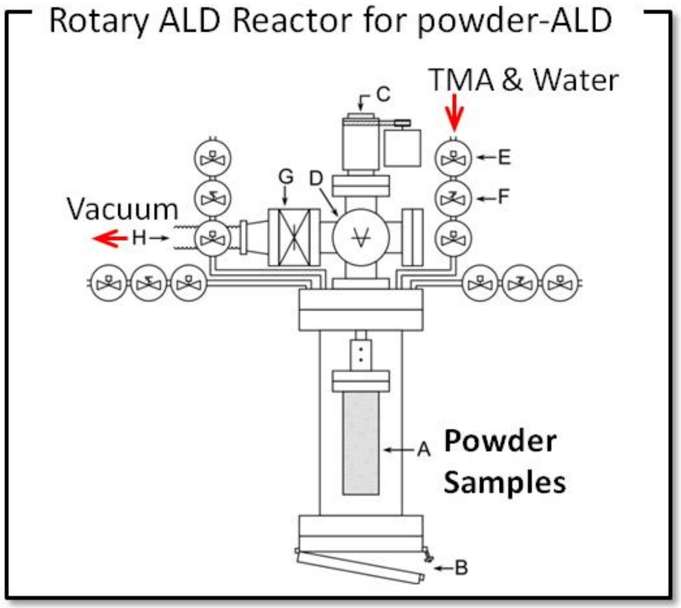
L.A. Riley, A.S. Cavanagh, S.M. George, S-H. Lee and A.C. Dillon, *Electochem. Solid State Letters* 14 (2011) A29.

Particle Coating by ALD

Fluidized Bed Reactor







Fluidized Bed Reactor (~ kg scale)
Rotary Powder Reactor (10's of grams)