NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Impact of ALD Coating on Mn-rich Cathode Materials



Shriram Santhanagopalan
Center for Transportation Technologies and Systems
National Renewable Energy Laboratory

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Overview

Timeline

Project Start Date: 06/01/2012
Project End Date: 05/31/2013
Percent Complete: 70 %

Budget

Total Project Funding: $110k
DOE Share: $110k
Contractor Share: N/A

Funding Received in FY12: $110k

Funding for FY13: $0

Barriers

- **Barriers addressed:**
  - Capacity fade during cycling of Mn-rich cathode materials at high temperatures
  - Scale-up issues associated with Atomic Layer Deposition

Partners

- Mohamed Alamgir (LGCPI)
- Karen Buechler, David King (ALD NanoSolutions, Broomfield, CO)
- Chunmei Ban and Rob Tenent (NREL)
- Se-He Lee (University of Colorado)

Relevance and Objectives

- The Advanced Battery Research (ABR) program identified manganese rich cathode as an attractive candidate for vehicle batteries. This material offers several benefits, including a wider operating window and higher energy density.
- One of the major limitations of this material pertains to cycle life.
- LG Chem Power Inc. (LGCPI) and NREL have previously conducted a scoping study on coating Mn-rich cathodes with oxides of alumina, which provided useful indicators to improving cell performance:
  - Atomic Layer Deposition (ALD) coating mildly reduced power capability
  - Improvement in cycling due to coating is significant when applied to Mn-rich cathode
  - Anode coating did not bring about much of an improvement
- With this background, LGCPI and NREL jointly proposed to assess the scalability of the ALD coating technique on Mn-rich cathode material as well as sheets of electrodes.
- **The objectives of this effort are:**
  - To evaluate the scalability of ALD coatings on large batches of Mn-rich cathode (from LGCPI) at a pilot-scale to improve rate capability, life, and abuse tolerance of this material.
  - To assess the feasibility of coating electrodes using the ALD technique

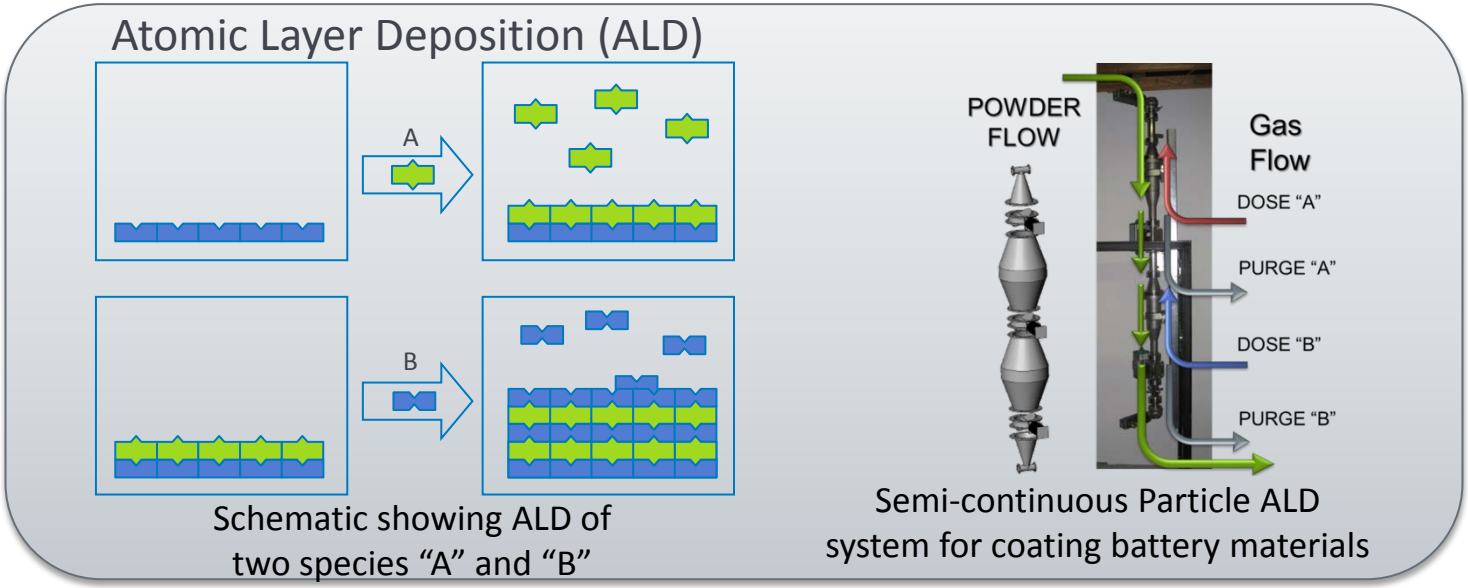
Milestones

Month/Year	Milestone or Go/No-Go Decision	Description	Status
Oct. 2012	Milestone report titled “Impact of ALD Coating on Mn-rich Cathode Materials”	• NREL and ALD Nanosolutions built a subcontract in place to coat cathode powders and electrodes • Two baseline samples were coated to produce four different batches of coated material	Complete
Dec. 2012	NREL to fabricate cells from baseline and coated samples for screening	• Coin cells were fabricated using both the baseline and coated materials to down-select coating conditions for the second round	Complete
Mar. 2013	NREL to ALD coat electrode samples with help from subcontractor	• ALD Nanosolutions modified coating reactors to include sheet samples • Electrodes for large-format (5”x5”) pouch cells were coated	Complete
June 2013	LGCPI to evaluate performance of coated powders and electrodes	• LGCPI will fabricate pouch format cells to evaluate improvements in cycling performance against the baseline cathodes	On Track

Approach/Strategy

- LGCPI and NREL built upon the success of the lab-scale work to demonstrate the benefits of the ALD technique to evaluate the scalability of the ALD coating process and the benefits of ALD coatings for long-term cycling and calendar life.
- As part of the scalability assessment, direct coating of electrode sheets was implemented, and the results was compared to coating active material powders to fabricate electrode sheets in a subsequent step.
- To accomplish these steps, NREL obtained bulk quantities of manganese-rich cathode powder and electrode sheets and coat the samples with help from a subcontractor (ALD Nanosolutions).
- The coating parameters were optimized using screening tests carried out at NREL, which included fabrication of coin cells from those samples.
- The powders and electrodes coated under revised conditions are currently being evaluated by LGCPI in large-format pouch cells.

Particle ALD™: Basics of Atomic Layer Deposition



Schematic showing ALD of two species "A" and "B"

Semi-continuous Particle ALD system for coating battery materials

- ALD is a sequential self-limiting gas-phase surface reaction.
- Film thickness is controlled by the number of cycles.

Schematics Credit: David King, ALD Nanosolutions

ALD is well established

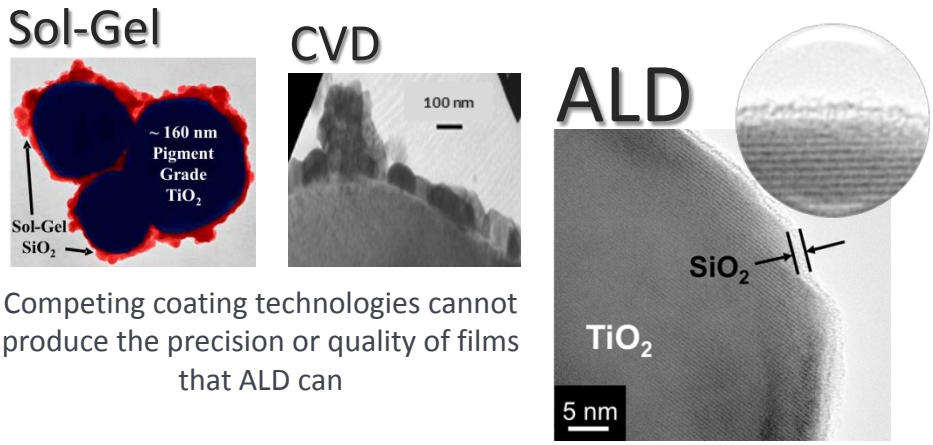
- Common in semiconductor industry
- Various applications for coating 3D objects
- Commercial reactors available

How to coat large batches of individual particles?

✓ **Fluidized Bed Reactor (FBR)**

- Gas flow fluidizes bed of particles
- Excellent mixing and heat transfer
- High surface area particles – coated conformally
- Industrially scalable technology

Unrivaled Particle Encapsulation

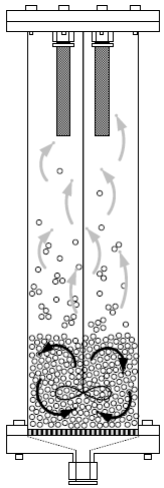


Competing coating technologies cannot produce the precision or quality of films that ALD can

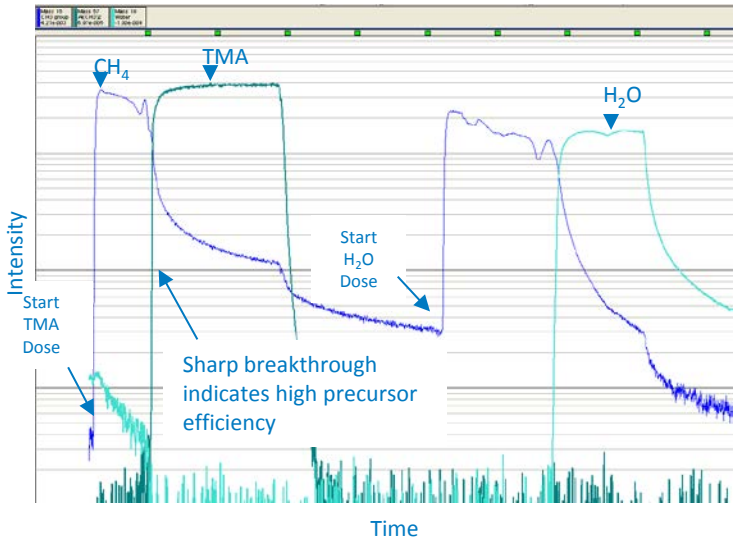
Technical Accomplishments: Particle ALD™ at ALD NanoSolutions

ALD NanoSolutions has the capability to process multiple batch size of powders in three separate reactors which scale the Particle ALD™ coating from 10s of grams to 10s of kg batches.

The existing ALD FBR reactor can process up to 8L of powder per batch



Figures Credit: Marcus Groner, ALD Nanosolutions



Chemical Efficiency of a typical ALD FBR Process: Batch reactors use in-situ process monitoring with a Residual Gas Analyzer. The calibration curve shown above is used to assess efficiency of the-coating process

Process Steps:

1) Load bed of powders into Fluidized Bed Reactor (FBR)
2) Fluidize powders at coating temperature and pressure
3) Sequentially introduce ALD precursors A-purge-B-purge
4) Repeat 3 for desired number of cycles

Two baseline samples were coated to produce 4 different batches of coated active material.

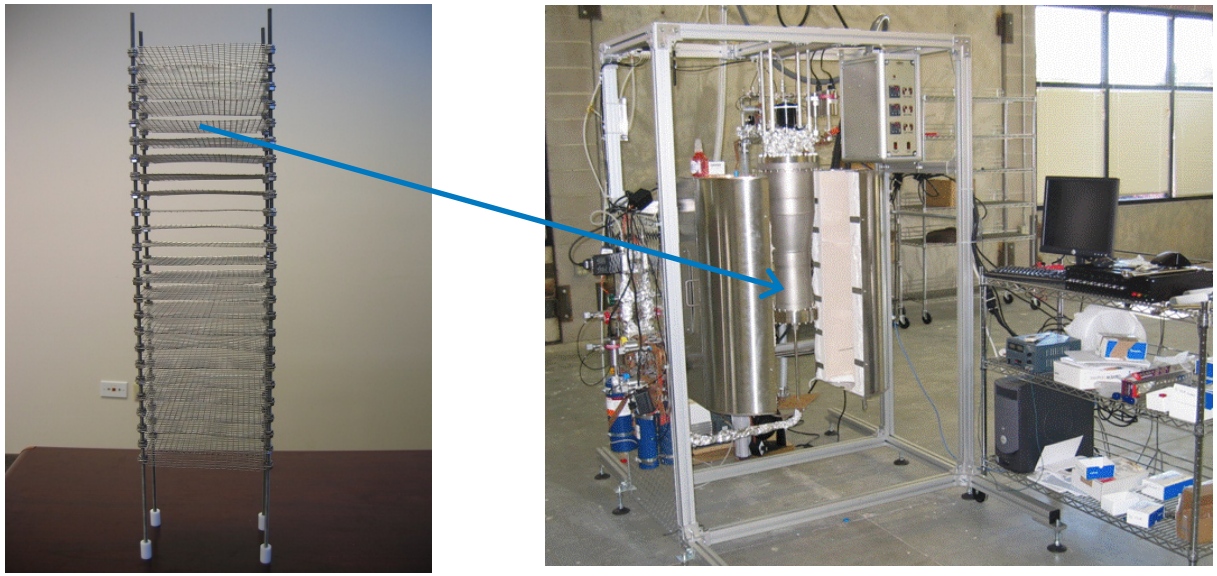
Technical Accomplishments: Electrode Coating at ALD NanoSolutions

In addition to a small-volume traditional flats ALD reactor and developing roll-to-roll ALD coating, ALD NanoSolutions can install a holder for carrying out ALD onto a large number of flats into the large-volume ALD particle reactors.

All Photos Credit: Marcus Groner, ALD Nanosolutions

In the FY12 phase of the work with ALD NanoSolutions, NREL subcontracted the installation of an electrode-rack to facilitate this reactor modification process.

An electrode holder for up to 25 electrodes of 6”x6” size was devised for ALD coating sheet electrodes directly.



Electrodes of 6” x 6” size will be coated directly using the holder build under NREL subcontract. Coating of Mn-rich NMC material underway.

Process Steps:

1) Load reactor with electrodes
2) Bring reactor to coating temperature and pressure
3) Sequentially introduce ALD precursors A-purge-B-purge
4) Repeat three for desired number of cycles

Sheet samples of the Mn-rich cathode were coated using the modified reactors for fabrication and evaluation of large-format pouch cells at LGCPI .

Technical Accomplishments: Initial Results

Chemical Stability:

- Check for chemical stability by storing the ALD-coated samples in the electrolyte at 60°C did not show any abnormal gassing.

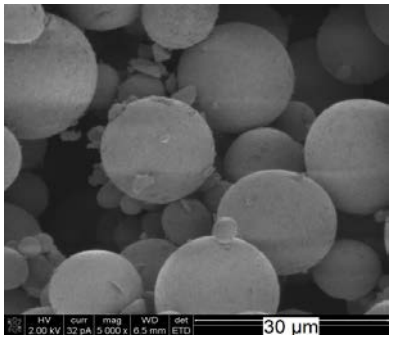
Al_2O_3 Content	2 Cycle	5 Cycle
LGC-HM-01	0.98%	1.86%
LGC-HM-02	1.12%	1.91%

Weight percentages of Al_2O_3 coating

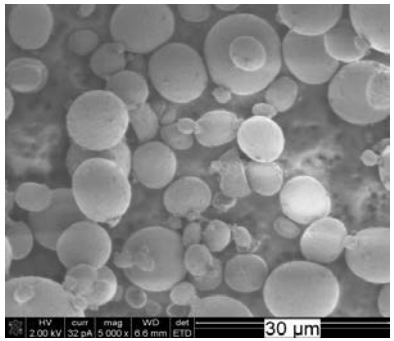
SEM Images:

- The coatings on both types of particles show good uniformity.
- The alumina on LGC-HM02 tends to flake off readily (perhaps due to a different surface treatment on the baseline particles).
- No performance issues were observed due to the flakes, indicating that this is essentially a processing difficulty.
- Tailoring the surface properties of the coatings to match those of the baseline material will help overcome such issues.

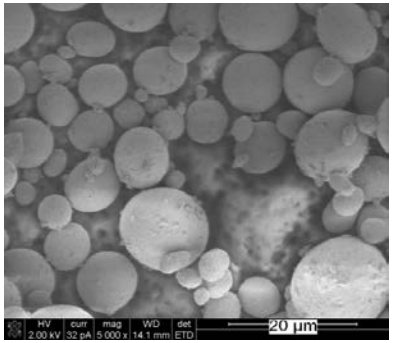
SEM Images Credit: Bobby To, NREL



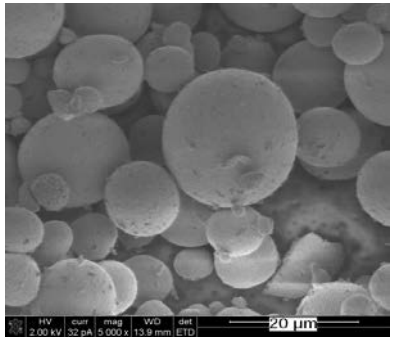
Sample - 1 (Baseline)



Sample - 1 (Coated)

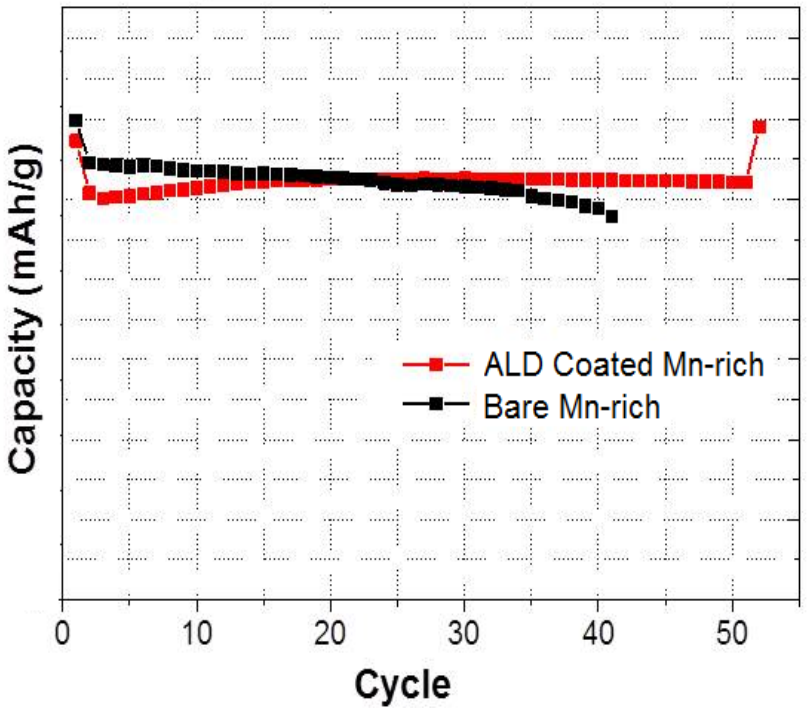


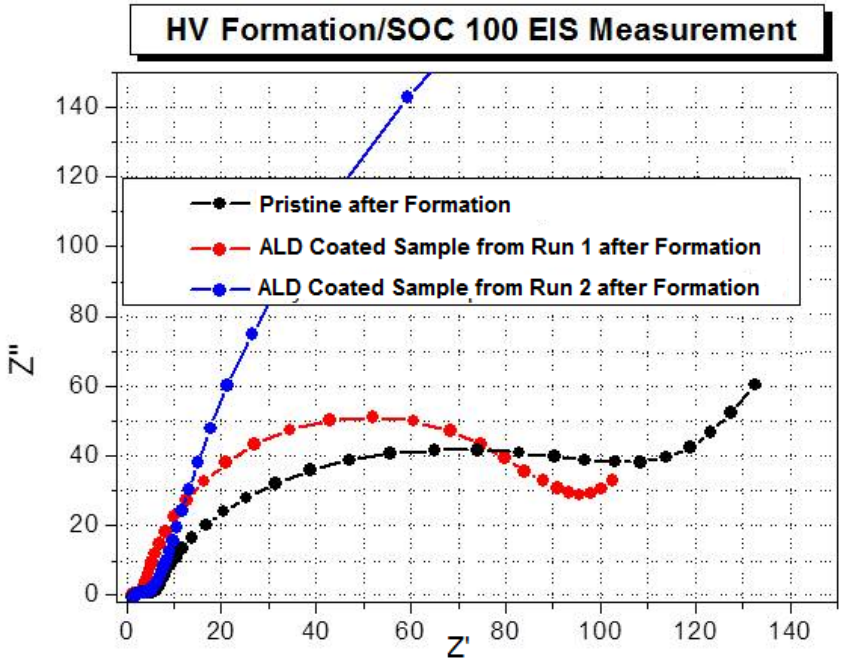
Sample - 2 (Baseline)



Sample - 2 (Coated)

Technical Accomplishments: Cell Evaluation





Figures Credit: Mohamed Alamgir, LGCPI

- During the initial evaluation, the coated sample showed almost no degradation after fifty 100% Depth of Discharge (DOD) cycles between 4.4 and 2.75 V, whereas the baseline sample showed a decline in capacity.
- Some rate-limitations were observed at higher C-rates; an increase in the impedance was also noticeable.
- These issues are addressed in the subsequent coating trials by selecting the coating parameters to match target performance.
- There were no noticeable variability in coating the different batches indicating no limitations in scaling from lab-scale to the pilot scale.

Collaboration and Coordination with Other Institutions

- NREL and LGCPI have collaborated over several years in building Atomic Layer Deposition as a viable technique to improve the safety and cycling performance of lithium battery materials.
- This project actively leverages prior work by the two teams to address a performance limitation that will enable use of the manganese-rich material for use in automotive batteries.
- ALD Nanosolutions is a pioneer in developing the atomic layer deposition process and has rapidly transitioned lab-scale results to the industry in multiple disciplines.
- The Energy Storage group at NREL also has an ongoing collaboration with the University of Colorado at Boulder in screening the coating and test conditions.

Proposed Future Work

- This was a short-term, fast-track project (total duration: one year)
- For the remainder of the performance period, the team will continue on-going efforts in the following areas:
    i) Evaluating coating of powders versus coating of electrodes
    ii) Testing of large format cells fabricated using the ALD-coated electrodes
- The final milestone will focus on delivering cell-level test results from LGCPI

Future work Pending Support:

- Continue to evaluate functional ALD coatings, working with NREL's ALD team
- Fine-tuning ALD attributes such as material composition and conductivity across the coating, as well as correlating these target properties with the deposition conditions will provide better control over the process.
- Future support will help identify the process-knobs to build functional coatings at the production scale.
- A semi-continuous production option has been validated at ALD Nanosolutions for large-scale manufacturing; future support will help transition this effort into a continuous, in-line coating step integrated with the cell-fabrication process.

Summary

- Pilot-scale ALD coating of Mn-rich cathode powders and electrode sheets were successfully demonstrated.
- Initial evaluation results indicate that better cycling performance over the baseline material.
- Our studies show that the atomic layer deposition technique is quite scalable with the cathode powders.
- A semi-continuous production option has also been validated for large-scale manufacturing and will facilitate industry adoption.
- Large-format cell testing is currently underway.
- The unique talent at ALD Nanosolutions, expert guidance from LGCPI and insight from University of Colorado at Boulder have come together to help NREL deliver a reasonable solution for this fast-paced project.