Impact of ALD Coating on Li/Mn-rich Cathode Materials




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

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: None

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

Relevance

- The ABR program has 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 for this material pertains to cycle life.
- LGCPI & NREL have previously conducted a scoping study on coating Mn-rich cathodes with oxides of alumina, which provided useful indicators to improving cell performance:
  - 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 & 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 re-affirm the benefit of coating of LG Chem Power Inc. (LGCPI) cathodes with ALD to improve their rate capability, life, and abuse tolerance of electrodes, at a pilot-scale.
  - To assess the feasibility of coating electrodes using the ALD technique.

Milestones

Month / Year	Milestone or Go/No-Go Decision	Description	Status
M1/Y1 (June 2012)	Receive baseline active material	• NREL received two different batches of baseline cathode material (powder) and sheet electrodes for ALD coating.	Complete
M6/Y1 (Dec. 2012)	NREL to ALD coat powder samples with help from subcontractor	• NREL and ALD Nanosolutions built a sub-contract in place to coat cathode powders and electrodes • Two baseline samples were coated to produce 4 different batches of coated material	Complete
M6/Y1 (Dec. 2012)	NREL to fabricate cells from baseline and coated samples for screening	• Coin cells were fabricated using both the baseline and coated materials; results discussed in slides below were used to down-select coating conditions for the second round	Complete
M9/Y1 (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” x 5”) pouch cells were coated	Complete
M12/Y1 (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	In Progress

Approach/Strategy

- LGCPI and NREL will build upon the success of the lab-scale work to demonstrate the benefits of the atomic layer deposition (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 will be implemented; and the results compared to coating active material powders to fabricate electrode sheets in a subsequent step.

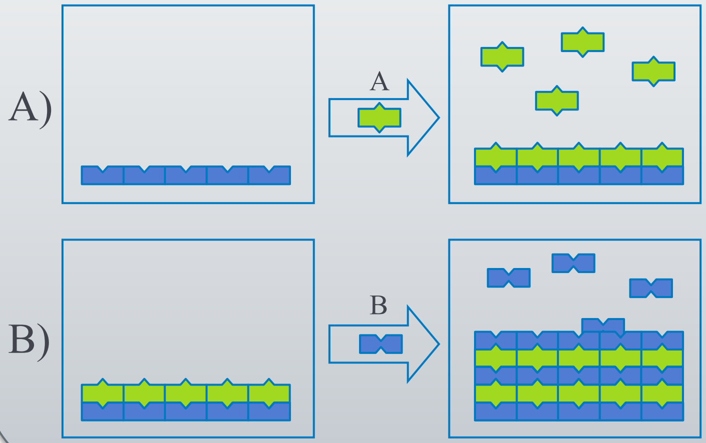
- To accomplish these steps, NREL will obtain bulk quantities of manganese-rich cathode powder and electrode sheets and coat the samples with help from a subcontractor (ALD Nanosolutions).

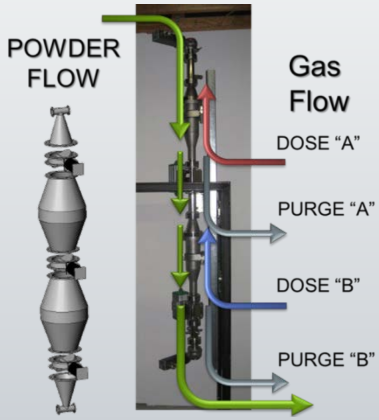
- The coating parameters will be optimized using screening tests carried out at NREL which include fabrication of coin cells from those samples.

- The powders and electrodes coated under revised conditions will be evaluated by LGCPI in large format pouch cells.

Particle ALD™: Basics of Atomic Layer Deposition

Atomic Layer Deposition (ALD)





Semi-continuous Particle ALD system for coating battery materials

Schematics Credit: David King, ALD Nanosolutions

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

ALD well established

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

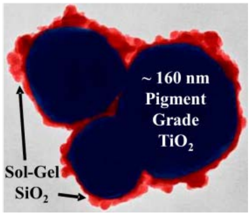
How to coat large batches of individual particles?

✓ **Fluidized Bed Reactor (FBR)**

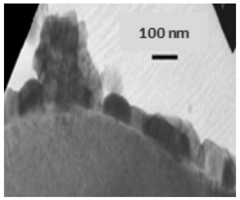
- Gas flow fluidizes bed of particles
- Excellent mixing and heat transfer
- High surface area particles – coated conformally
- Industrially scalable technology

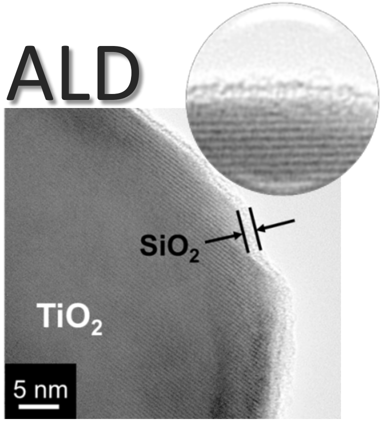
Unrivaled Particle Encapsulation

Sol-Gel



CVD



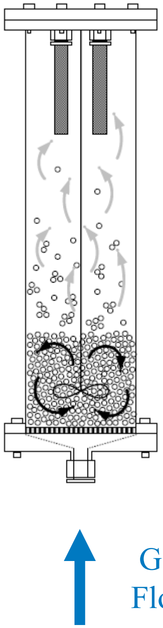


Competing coating technologies cannot produce the precision or quality of films that ALD can

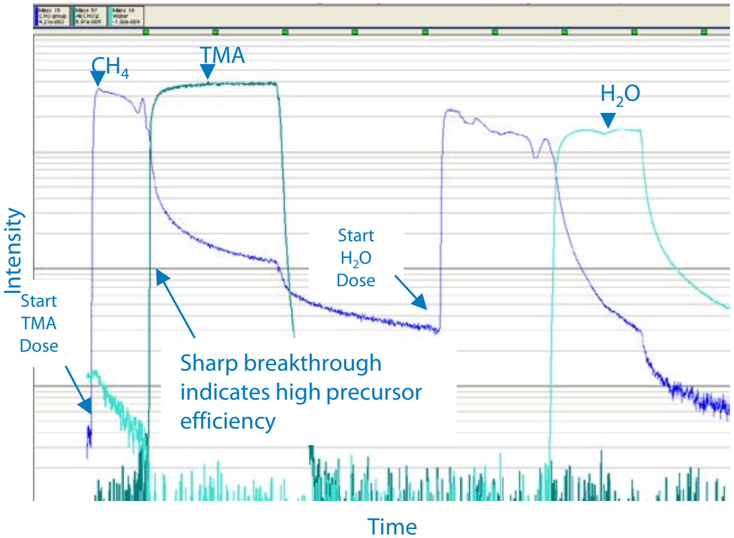
Particle ALD™ at ALD NanoSolutions

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.

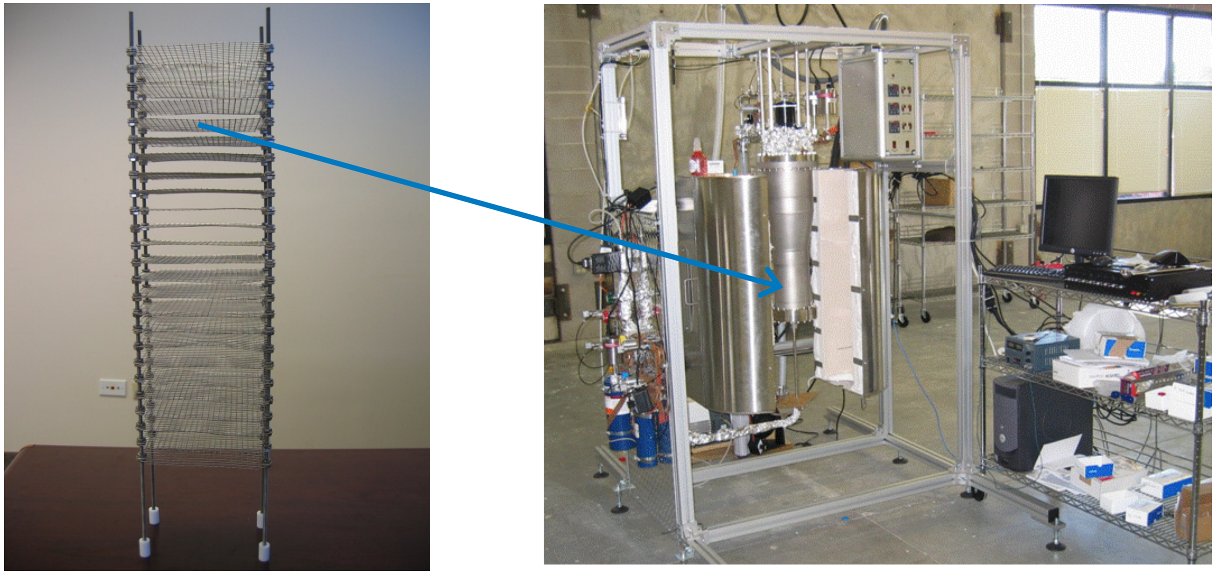
Electrode Coating at ALD NanoSolutions

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.

Figures Credit: Marcus Groner, ALD Nanosolutions

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

An Electrode Holder for up-to 25 electrodes of 6” x 6” 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 3 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 .

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.

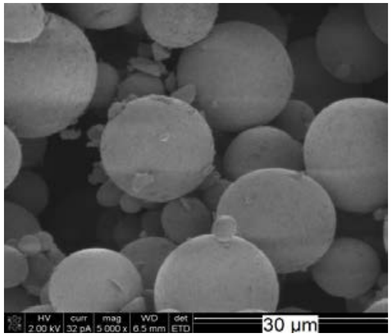
SEM Images:

- 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.

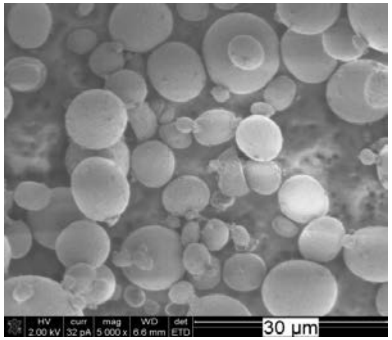
Al_2O_3 Content	2 Cycle	5 Cycle
LGC-HM-01	0.98%	1.86%
LGC-HM-02	1.12%	1.91%

Weight percentages of Al_2O_3 coating

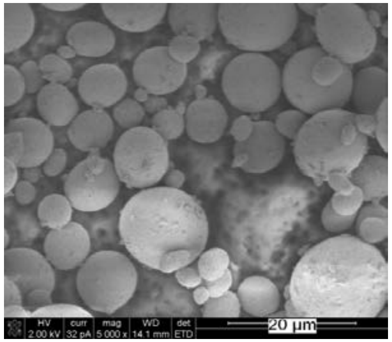
SEM Images Credit: Bobby To, NREL



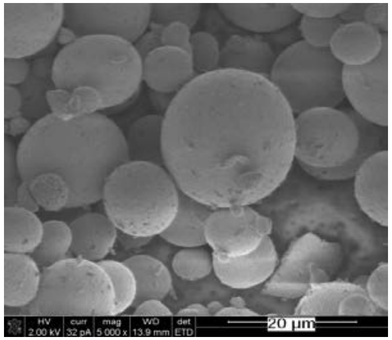
Sample - 1 (Baseline)



Sample - 1 (Coated)

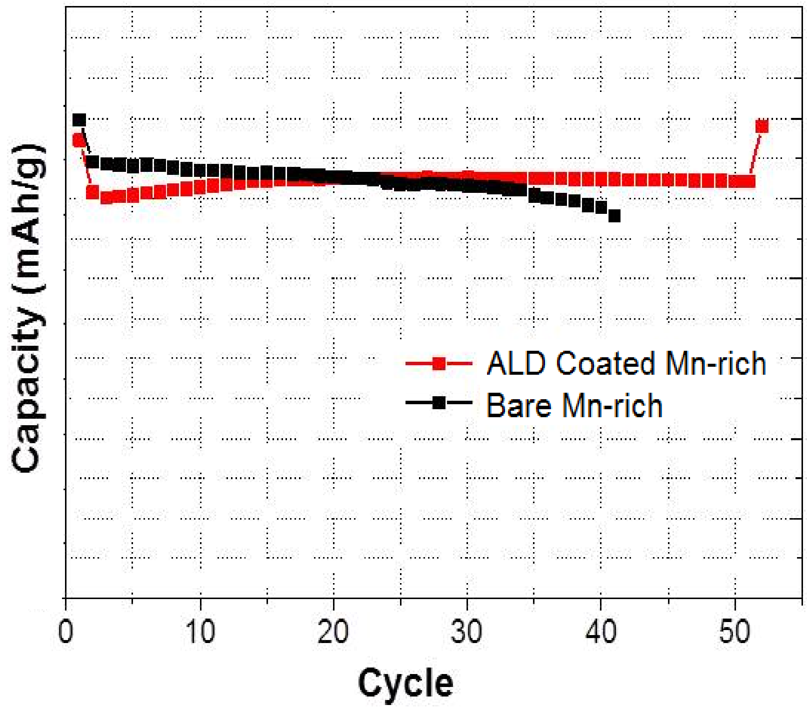


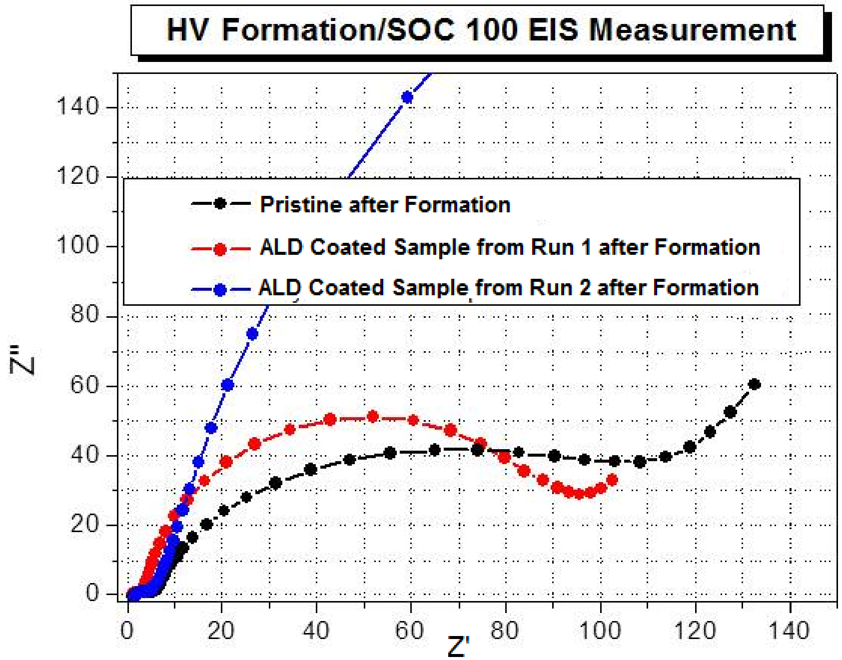
Sample - 2 (Baseline)



Sample - 2 (Coated)

Cell Evaluation





Figures Credit: Mohamed Alamgir, LGCPI

- During the initial evaluation, the coated sample showed almost no degradation after 50 100% 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.
- Initial phase of this work was guided by findings by the US-Drive team that identified the need to resolve the cycling issues at high temperatures. The US-Drive Team provides periodic feedback during review meetings.

Proposed Future Work

- This was a short-term fast-track project (total duration: 1 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 key milestone will focus on delivering cell-level test results from LGCPI

Future work Pending Support:

- 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

- The FY12 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.
- Pilot-scale ALD coating of Mn-rich cathode powders and electrode sheets were successfully demonstrated.
- Initial evaluation results indicate that good cycling performance over the baseline material.
- 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 on this fast-paced project.

Reviewer-Only Slides

(Note: please include this “separator” slide between those to be presented and the “Reviewer-Only” slides. These slides will be removed from the presentation file and the DVD and Web PDF files.)

Responses to Previous Year Reviewers' Comments

If yours is an on-going project that was reviewed last year, address 1-3 significant questions/ criticisms/recommendations from the previous year's reviewers' comments, available at: http://www1.eere.energy.gov/vehiclesandfuels/resources/vt_merit_review_12.html.

Last year's presentations can be found at: http://www1.eere.energy.gov/vehiclesandfuels/resources/proceedings/2012_merit_review.html.

This start date for this project was June 2012 and so we did not have any comments from reviewers in the previous year.

Publications and Presentations

- Robert Tenent, USDRIVE Electrochemical Tech Team Meeting at ANL - 24 January 2013.
- Shriram Santhanagopalan, Mohamed Alamgir, Karen Buechler and David King, Milestone Report titled *Evaluate ALD Coatings of LGCPI Cathode Materials and Electrodes*, Submitted October 2012.

Critical Assumptions and Issues

- This project was scoped out based-on some initial laboratory scale data on performance improvements from atomic layer deposition over cathode powders.
- The team assumes that the coating parameters optimized for the powders can be used for the sheet coating process with minor modifications.
- Uniformity of the large batch of coatings has been characterized at the material level only based on limited samples (e.g., using SEM or flue-gas analyses). Initial results from large-format cell testing indicate no limitations; but variations from one batch to another have not been characterized under the current effort.
- The coating process is fine-tuned ad hoc for each run; this process must be standardized.