Impact of Surface Coating on LMR-NMC Materials : Evaluation and Downselect

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Overview

Timeline

- Start: October 1, 2012
- End: Sept. 30, 2014
- Percent complete: 50%

Budget

- 100% DOE

Barriers

- Calendar/cycle life of lithium-ion cells

Partners

- Voltage Fade Team at Argonne
- *LBNL, ORNL, NREL, BNL, JPL*
- *Y.K. Sun (Hanyang University)*
- Toda, BASF

Project Objectives - Relevance

Voltage fade in lithium-, manganese-rich (LMR-NMC) oxides reduces energy density of lithium-ion cells on calendar–life and cycle–life aging

- Does surface modification help mitigate the material voltage fade?

Milestones

- Establish baseline material and test protocols to determine the extent of Voltage Fade — December 2012
- Establish baseline data on standard materials to facilitate comparison of various datasets — March 2013
- Obtain data to determine effect of surface modification on the material with Go/No-go decision — March 2013

Studying the coating effect on the voltage fade

Approach

- Changing the material surface by reduction or oxidation.

As the Mn oxidation state is very important during the first charge activation process, various atmospheres will be used in order to reduce the voltage fade or to force it to happen in the first cycle.

- Adding some electrolyte additives that can polymerize when the battery is cycling.

As the additive is incorporated into the electrolyte, no additional processing steps are required.

- Material coating.

Voltage Fade Baseline Material and Test Protocol

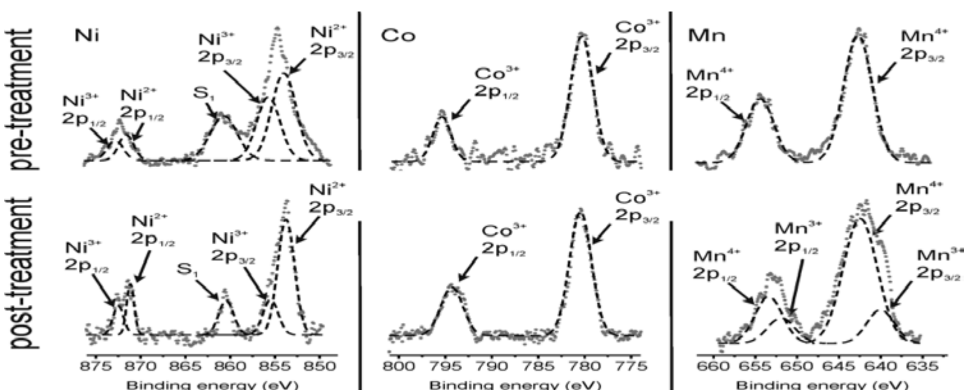
- Team chose a baseline material: **$0.5Li_2MnO_3 \bullet 0.5LiNi_{0.375}Mn_{0.375}Co_{0.25}O_2$**
  (well characterized positive electrode, available in large quantities)
- Cell configuration: oxide as positive, Li metal as negative

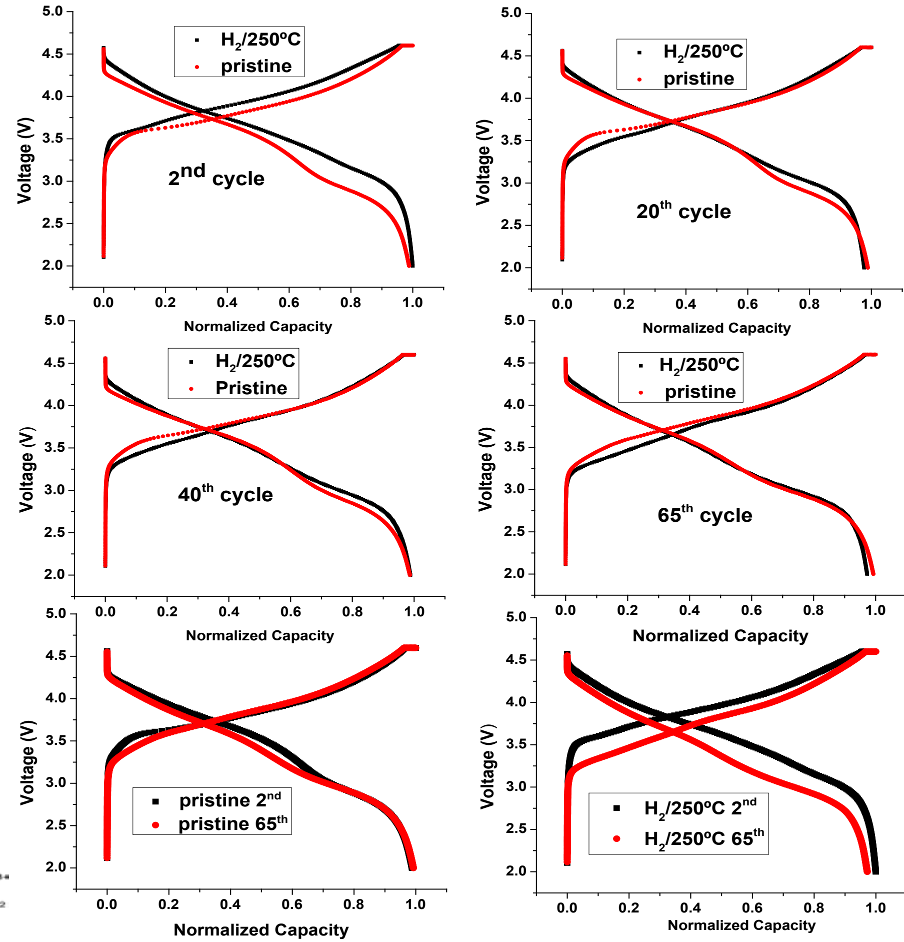
- Temperature: RT (also 30°C and 55°C)
- Initial activation cycle: 2-4.7V @ 10 mA/g
- Following cycling procedure: 2-4.7V @ 20 mA/g
- Total of 6 current interrupts implemented to obtain quasi-OCVs & DC cell resistances during charge at 3.5V, 3.9V, 4.3V, and during discharge at 4.0V, 3.6V, 3.2V.
  Each interrupt is a 10 minute rest.

- Number of cycles: 20
- Total test time (days): ~20
- Excel macro processes acquired data, collection in database (Ira Bloom, Argonne)

H_2 Reduction of the material Cycling and XPS of $LiNi_{0.15}Co_{0.1}Mn_{0.55}O_2$ material heated under H_2

- XPS shows a partial reduction of Mn^{4+} to Mn^{3+}. The voltage discharge plateau was enhanced by H_2 reduction as shown in the 2nd cycle.
- Enhance of the voltage in the 2nd cycle.
- Unfortunately, a huge voltage fade was observed with cycling and after 65 cycles the heated and pristine material provide similar discharge voltage plateau.
- No voltage fade effect was observed.



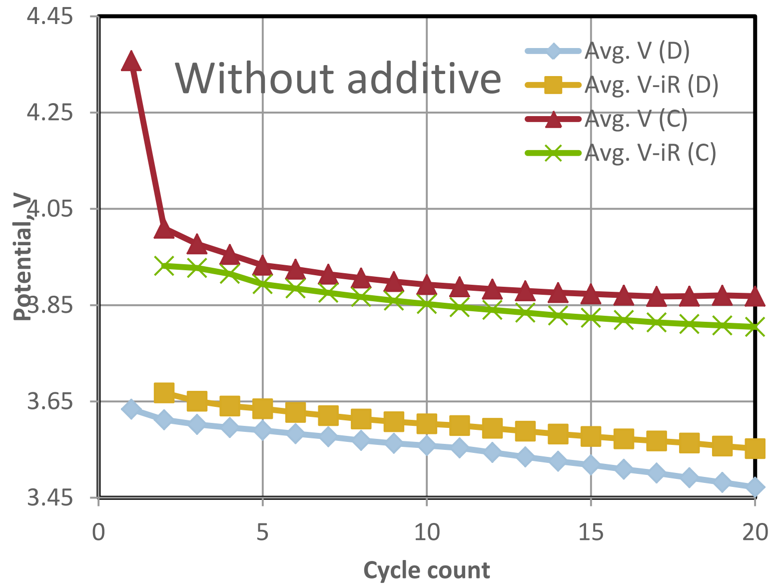


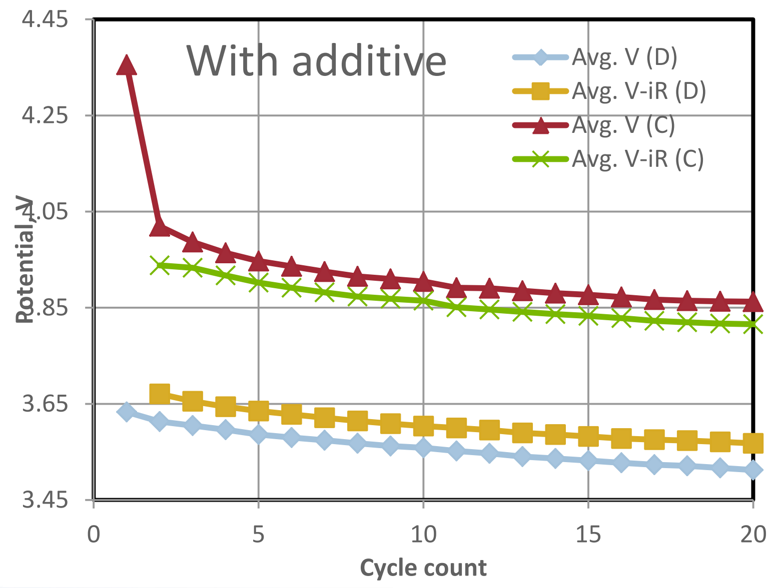
Cycling and XPS of $LiNi_{0.15}Co_{0.1}Mn_{0.55}O_2$

Effect of 3H-thiophene electrolyte additive on the voltage fade of HE 50/50 material

- The use of 3H-thiophene has a minimal effect on the cathode average voltage.

- 3H–thiophene electrolyte did not eliminate the voltage fade of HE 50/50 material.



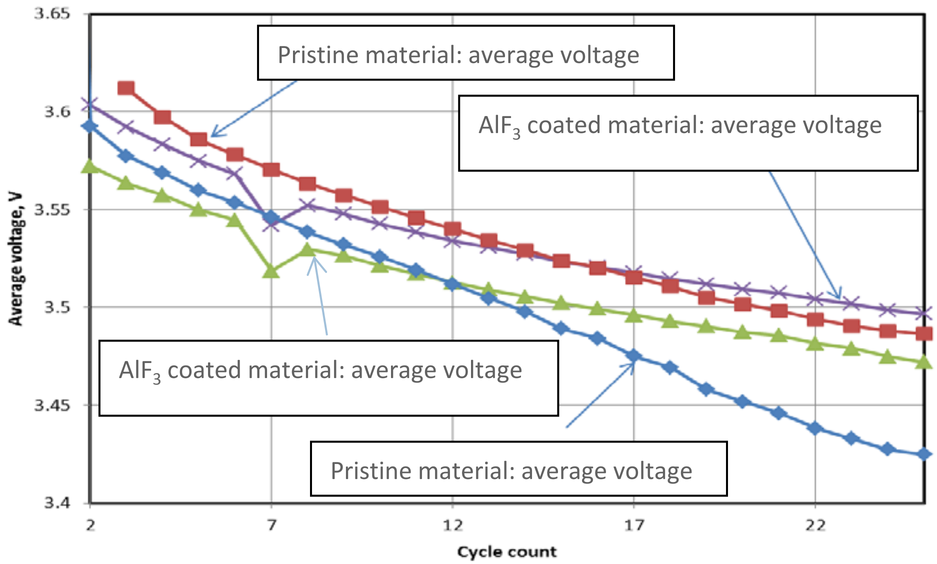


Effect of AlF_3 coating on the voltage fade of $Li_{1.2}Ni_{0.175}Co_{0.1}Mn_{0.525}O_2$ material

- Both materials show voltage fade.
- Small modification was observed with AlF_3 coating.
- The average discharge voltage fading :

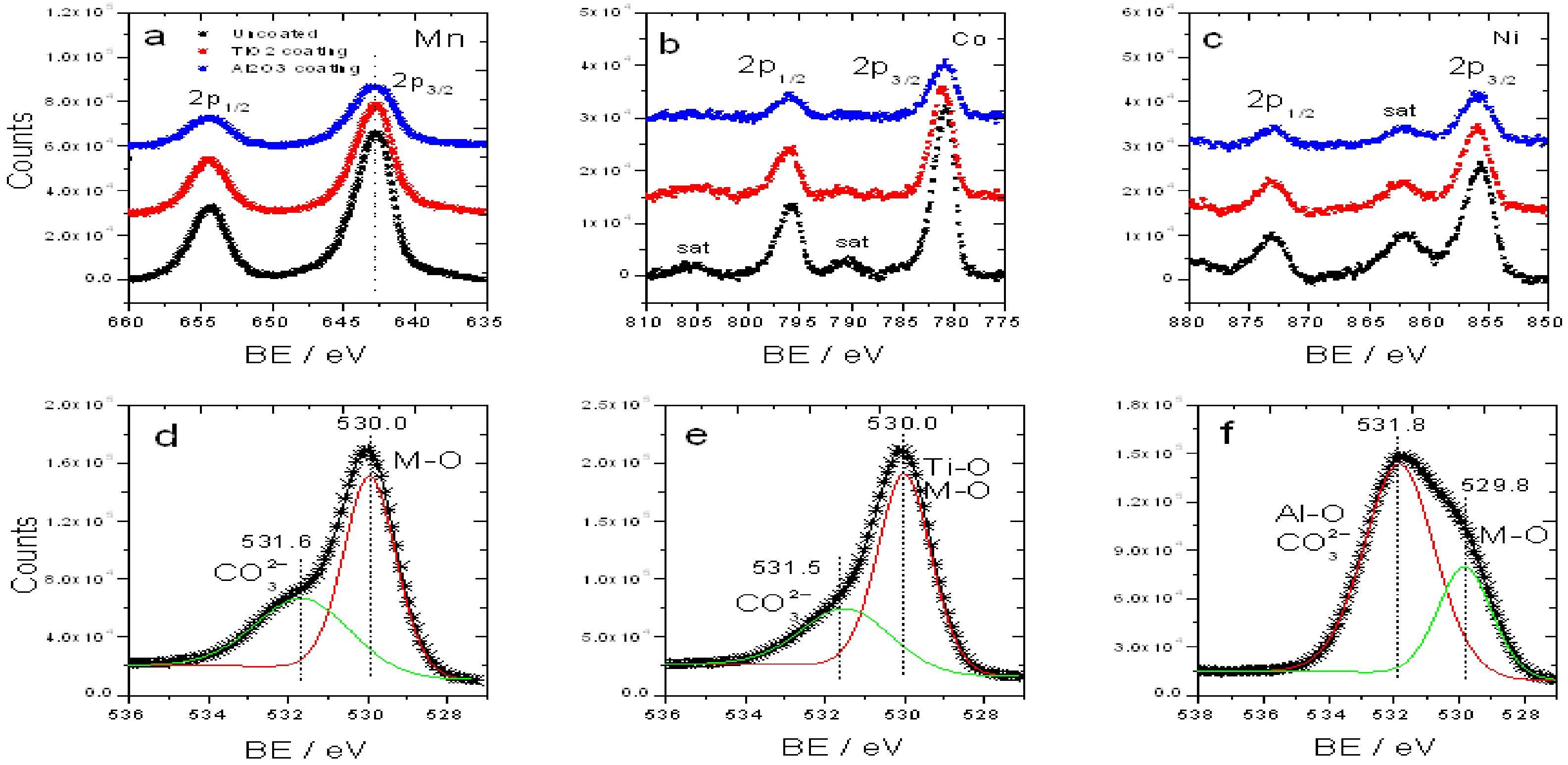
Based on the initial average voltage (when the impedance factor is included)

The coated sample and the pristine exhibit about 2.80% and 4.73% loss respectively.



ALD coatings of Toda HE5050

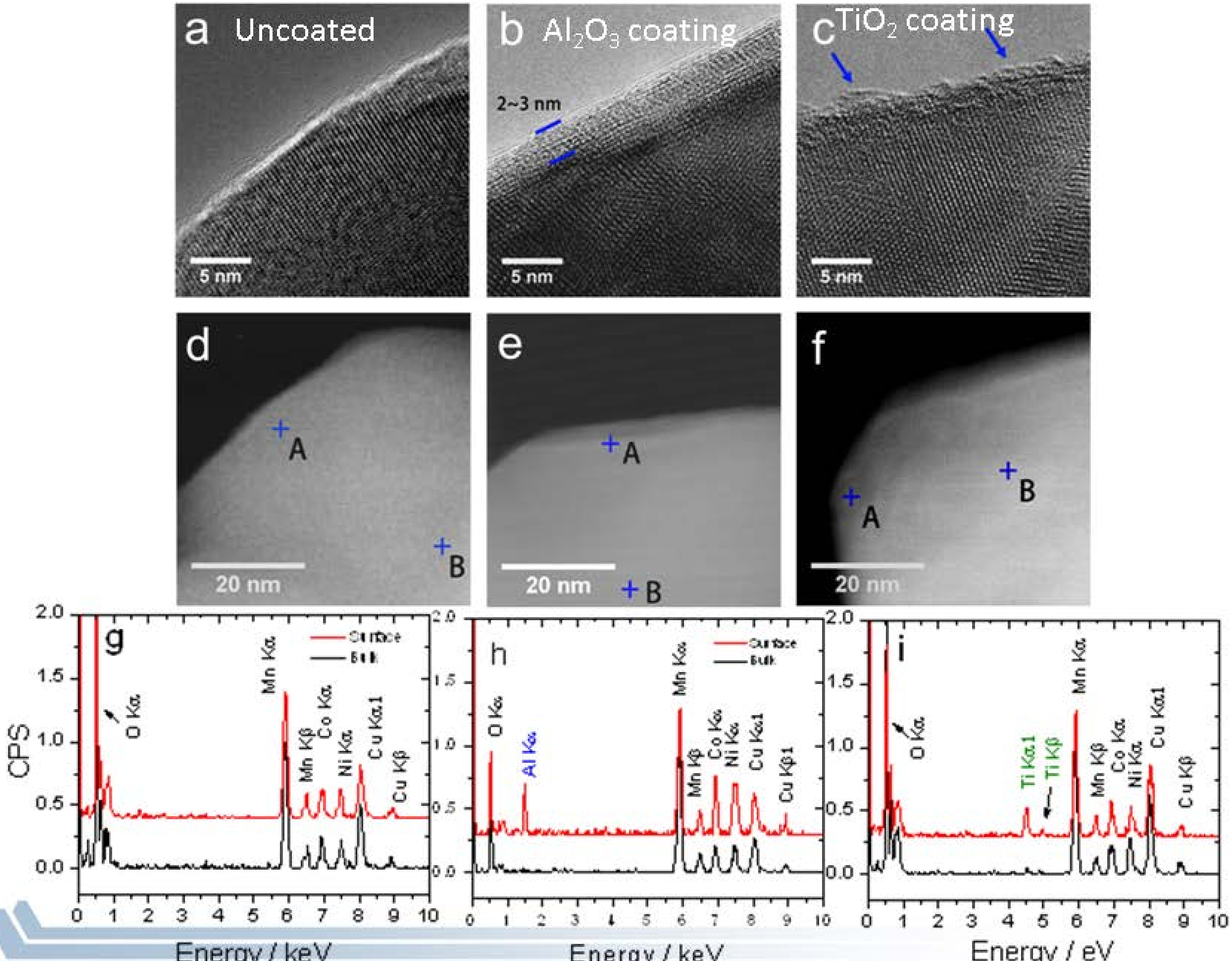
- Laminates and powder were coated with three different chemistries ZrO_2, Al_2O_3 and TiO_2 of atomic layer depositions and cycled in coin cells vs. lithium metal using the Voltage Fade Standard Testing Protocol.



XPS confirms Al_2O_3 and TiO_2 Coatings

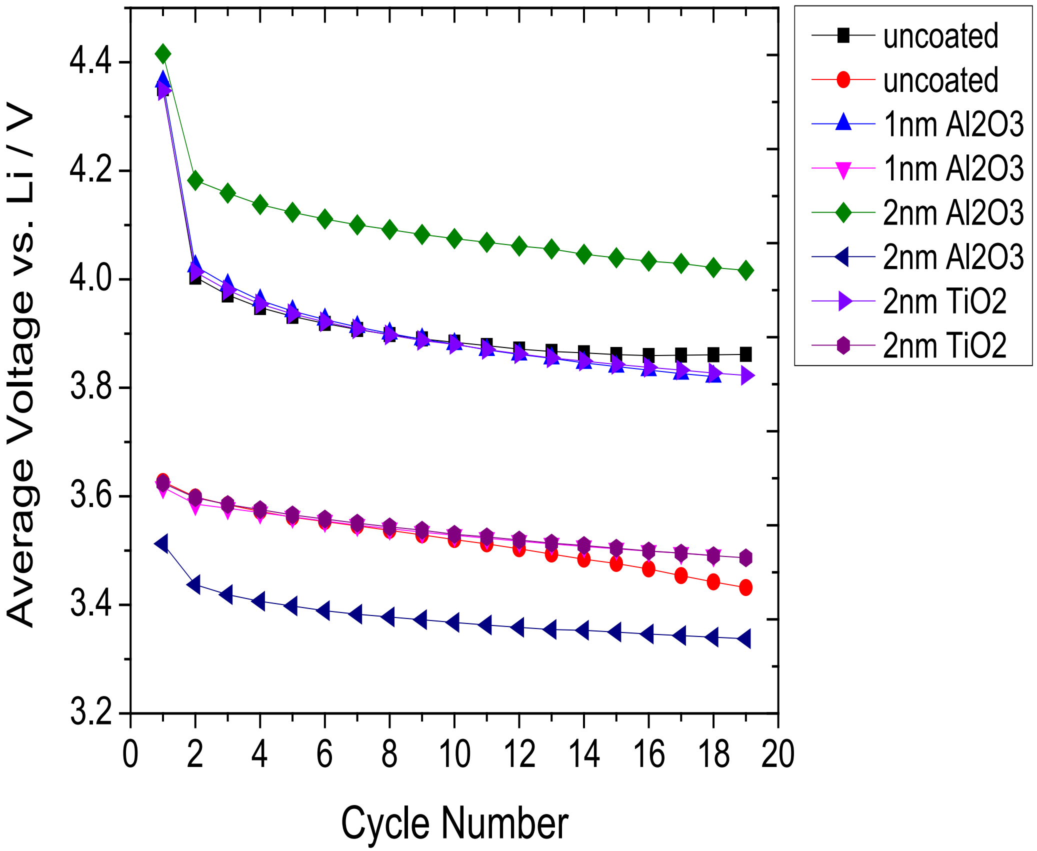
Coatings performed by X. Henry Meng and Jeff Elam (ES of ANL)

ALD coating is less than 3nm



ALD coatings of powder material : Toda HE5050

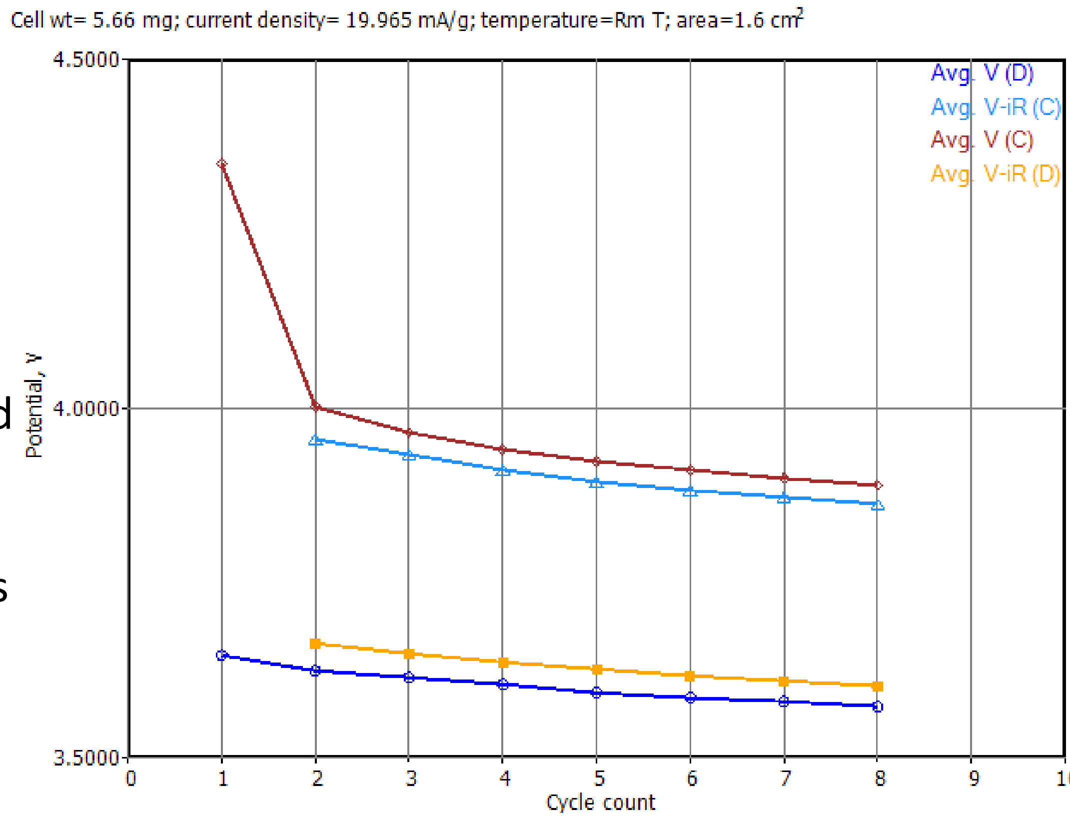
- ALD coating did not remove the voltage decay.
- 1nm Al_2O_3 and 2nm TiO_2 coating layers have comparable effect on the voltage stabilization. As the Al_2O_3 coating layer gets thicker, severe polarization can be observed.



ALD coatings of laminate electrode: Toda HE5050

- The chemical composition of the coatings was selected with considerations of ALD expertise and degree of oxidation of the transition metal present.

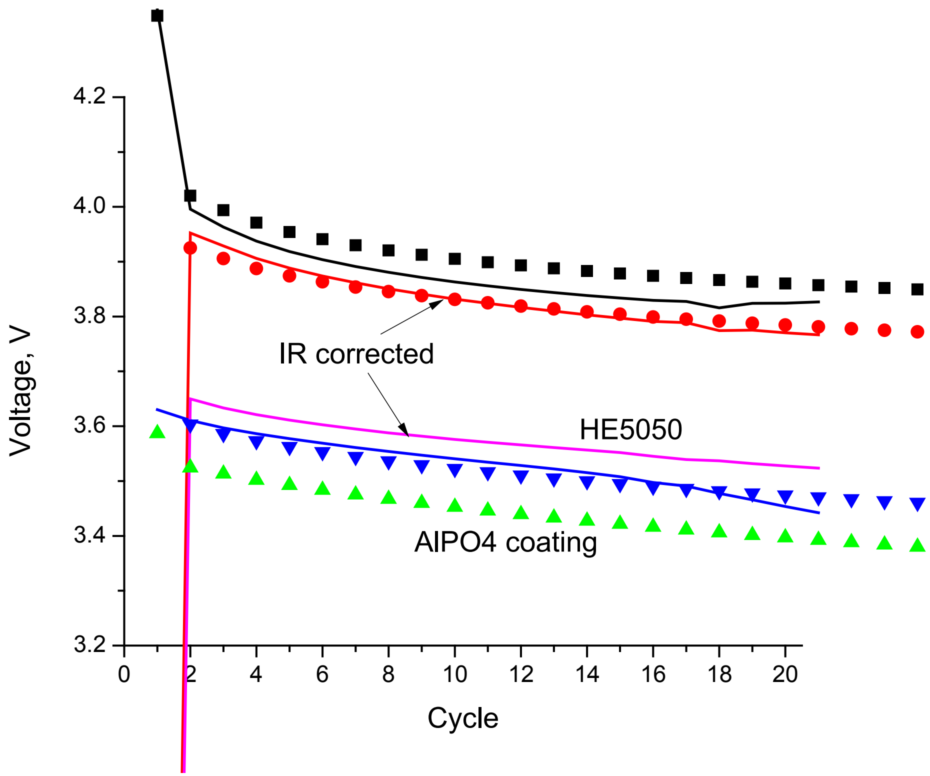
- The temperature of the coating could affect the properties of the binder. If the degree of voltage fade was reduced, uncoated "blank" laminates would be heated at the same conditions and tested in order to separate the effects of the coating from that of the heat treatment.



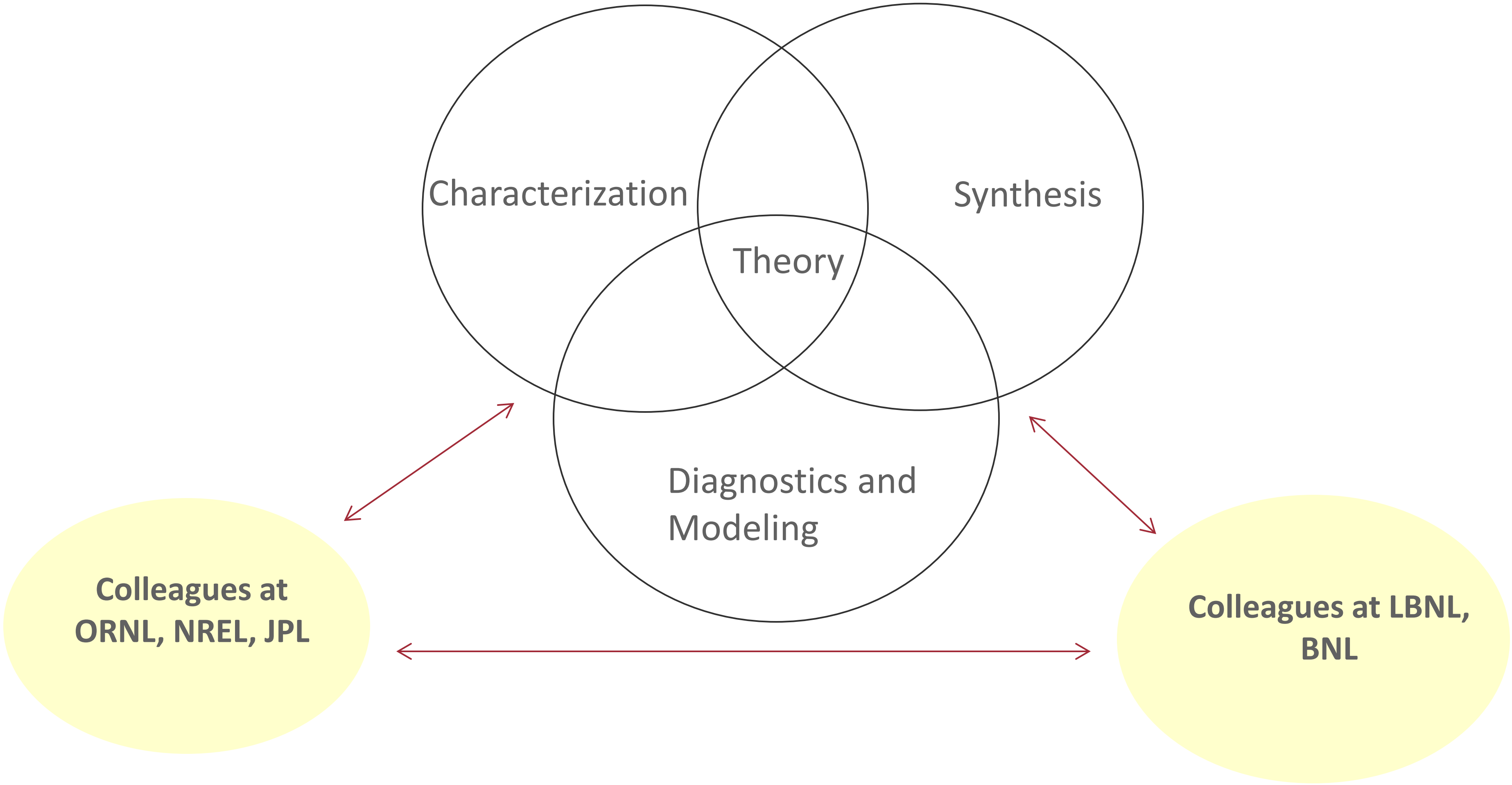
- As represented above by the TiO_2 100 ^oC example, none of the coatings tested to date have suppressed voltage fade. Blank heat-treated laminates do not appear necessary.

$AlPO_4$ coating of HE5050 material

- $AlPO_4$ coating did not remove the material voltage fade.
- Some polarization is observed with the coated material.

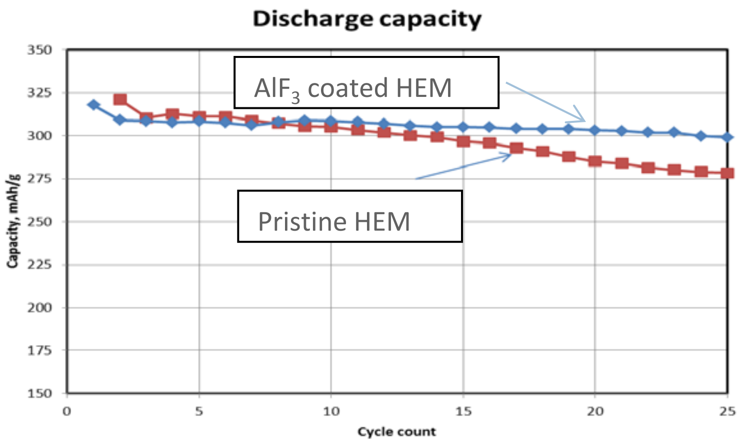


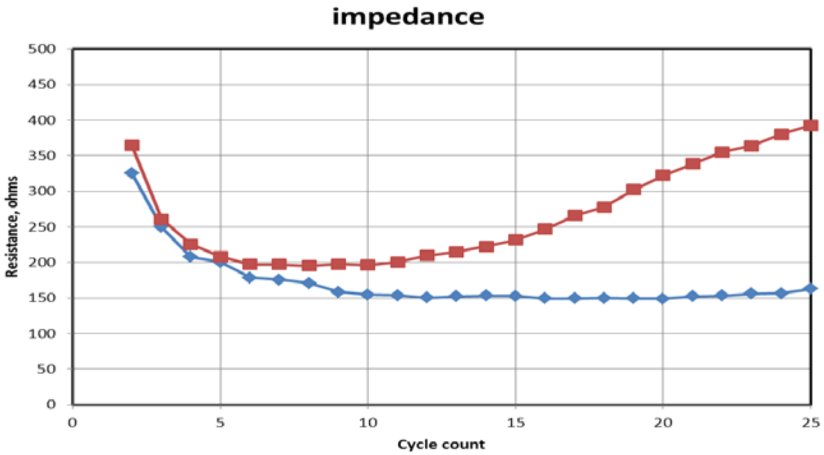
Collaborations



Summary

- Various surface modification are tested on the high energy cathode materials and especially HE 5050.
- The coating did not fix the voltage fade.
- The % of voltage fading in the 3.8 V may be related to the presence of Co and Mn/Ni ratio in the material.
- The coating helps keep the capacity and did not increase the battery impedance.





Future work

- No more VF coating will be performed.
- Synthetize few compositions with various Ni/Mn ratio and cobalt free materials.
- Substitute some Mn with Mg or Cr.

Acknowledgments

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