

# Atomic Layer Deposition for Stabilization of Silicon Anodes



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**Project I.D. # ES145**

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# Overview

## Timeline

- October 1, 2010
- September 30, 2014
- ~80%

## Budget

- Total project funding  
---100% by DOE
- Funding received:  
FY 2012 \$440 K  
FY 2013 \$440 K  
FY 2014 \$440 K

## Barriers: Strategy

**Cost:** Silicon is an inexpensive abundant element. Low-cost processing and commercially available materials are employed.

**Performance:** High gravimetric and volumetric capacity are achieved for the coated electrodes that exhibit durable cycling.

**Reversibility :** Elastic coatings are used to stabilize silicon anodes to enable highly reversible cycling.

## Collaborators

- |                          |                           |
|--------------------------|---------------------------|
| • Gao Liu, LBNL          | • Ji-Guang Zhang, PNNL    |
| • Phil N. Ross, LBNL     | • Chongming Wang, PNNL    |
| • Robert Kostecki, LBNL  | • Yue Qi, MSU             |
| • Perla B Balbuena, TAMU | • Xingcheng Xiao , GM     |
| • Kevin Leung, SNL       | • Dr. Anthony Burrell and |
| • Jason Zhang, PNNL      | Dr. Ira Bloom, ANL        |

# Main Objectives/Relevance

- Develop conductive, elastic and ultrathin coatings for electrode materials by using Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD);
- Stabilize the thick silicon anodes with the novel coatings to enable sustainable, highly reversible cycling performance;
- Investigate effects of the nanoscale surface modification on irreversible capacity loss, morphology and structural evolution during cycling.

## Addresses targets:

**Low-Cost:** Low-cost processing and commercially available silicon materials are employed.

**High-energy:** The elastic coatings with excellent mechanical properties enable thick silicon electrodes (high mass loading) sustainable cycling with high capacity.

**High efficiency:** MLD coatings are used to stabilize silicon anodes for highly reversible cycling.

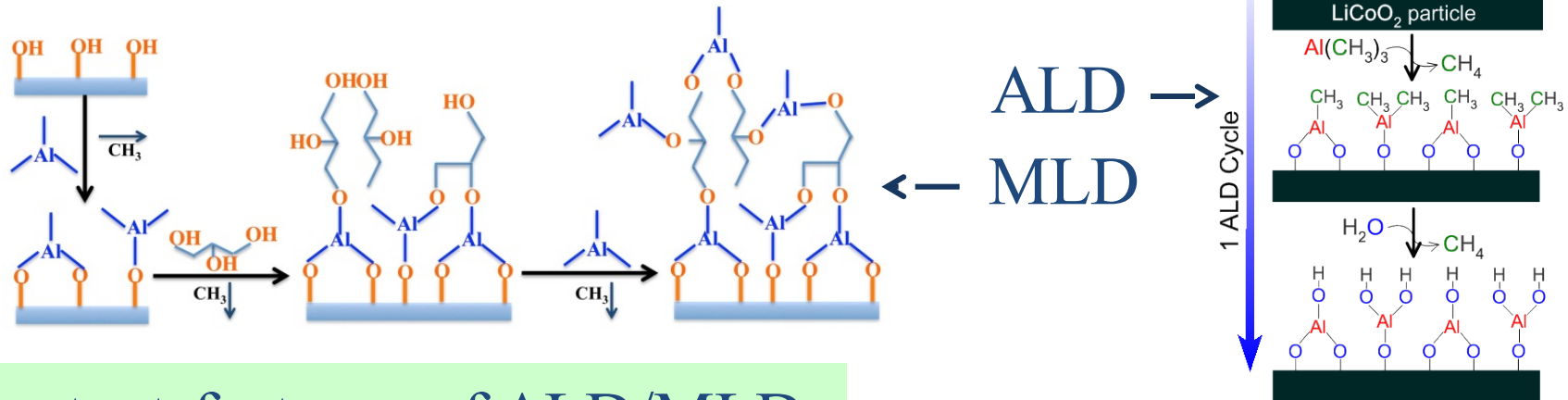
# Milestones

| Milestone  | Status      | Date       |
|--|-------------|------------|
| Characterize the effect of MLD coatings on the Si anodes, and demonstrate MLD-coated Si anode with reduced irreversible capacity loss at 1 <sup>st</sup> cycle | Complete    | July 2013  |
| Supply the optimized MLD-coated thick electrodes (>20um) to LBNL for verification  | Complete    | Sept. 2013 |
| Identify the effect of the alucone MLD coating on the structure and morphology of Si anodes during cycling.  | Complete    | Dec. 2013  |
| Develop aluminum oxide -carbon composite coatings by pyrolysis of alucone MLD TMA-GL films.  | Complete    | Mar. 2014  |
| Stop the development of aluminum oxide -carbon composite coatings if the coating cannot help the performance of Si anodes.                                     | On track    | June 2014  |
| Synthesis and characterize the novel LiAlF <sub>4</sub> or AlF <sub>3</sub> /Alucone hybrid coatings using ALD and MLD.  | In progress | Sept. 2014 |

# Approach/Strategy

## Technical Approach:

Apply ALD and MLD coatings on high-capacity Si anodes that enables significantly improved electrochemical performance.

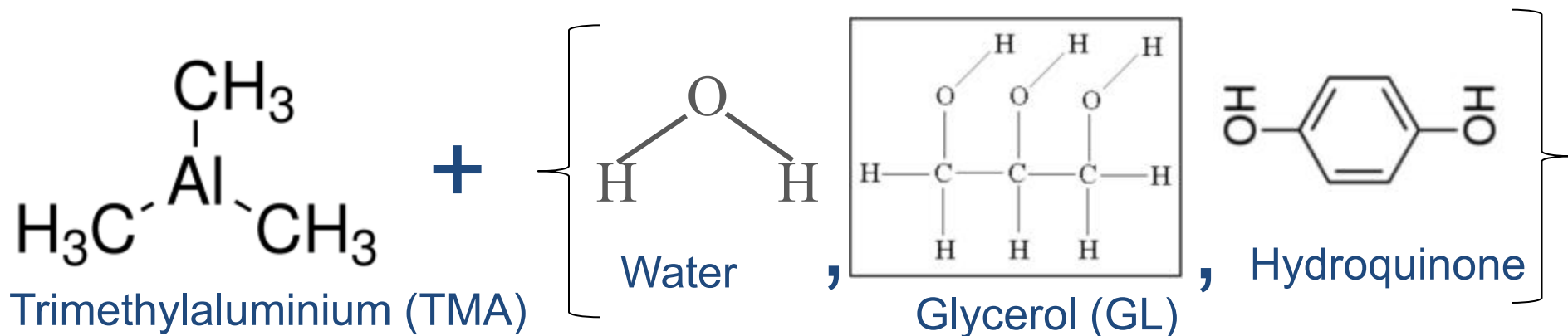


## Important features of ALD/MLD

- ❖ Sequential & self-limiting surface reactions enable **Conformal and atomic thickness control ( $\sim 1 \text{ \AA}$ )**;
- ❖ Especially powerful for 3-D nano complex architecture;
- ❖ **Commercially scalable** (No solvent, no excessive amount of precursors);
- ❖ Applicable to coat the materials with a variety of metal oxides, metals and organic/non-organic compounds coating.

# Approach/Strategy

➤ *Develop inorganic-organic hybrid coating with tunable mechanical properties*



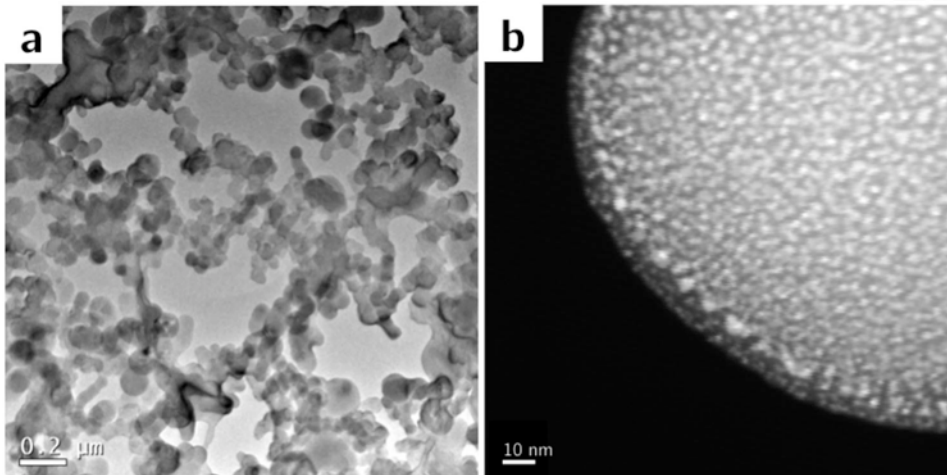
| Co-reactant with TMA | Density (g/cm <sup>3</sup> ) | Elastic modulus (GPa) | Hardness (GPa) | Conductivity                                | Stability |
|----------------------|------------------------------|-----------------------|----------------|---|-----------|
| water                | 3.0                          | 195                   | ~6.6           | Ion conductive in LiAlO <sub>2</sub>        | Great     |
| Glycerol             | 1.6                          | 39                    | ~(1.0)         | Ion and <i>e</i> conductive (Carbon domain) | Good      |
| Hydroquinone         | 1.6                          | 29.2                  | ~1.24          | Ion and <i>e</i> conductive (Aromatic ring) | Great     |



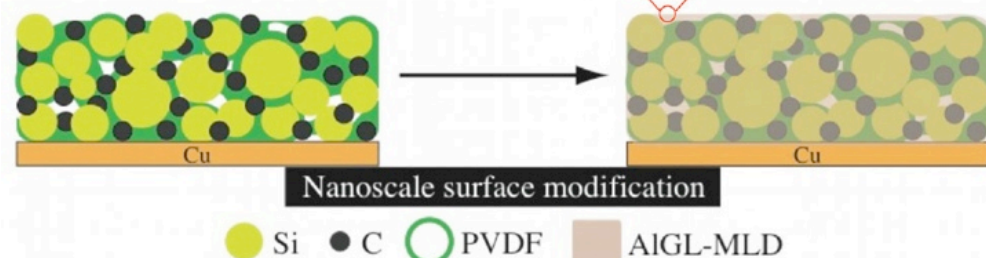
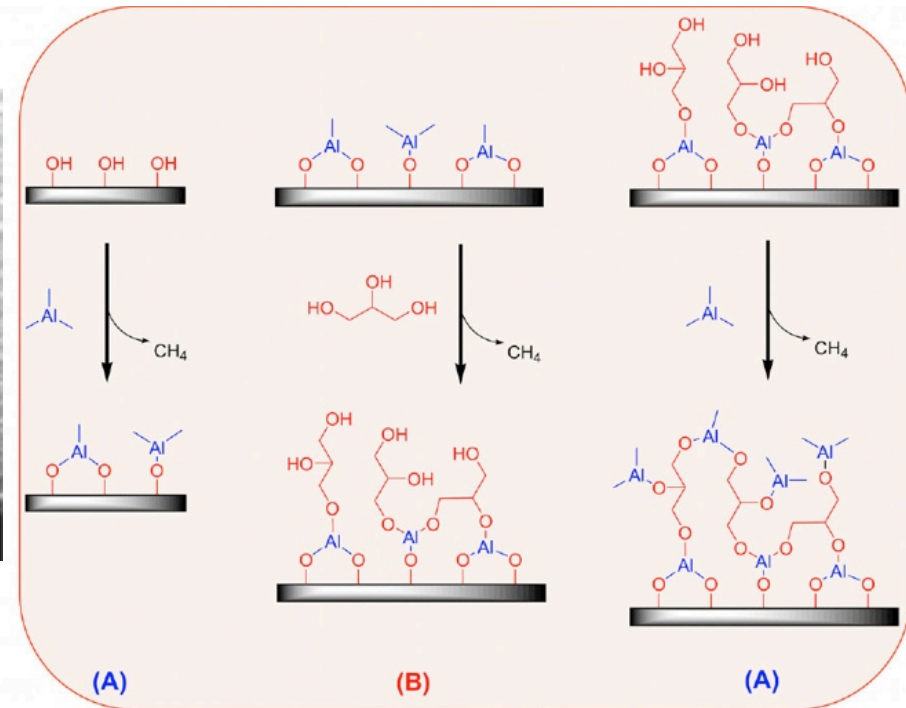
# Technical Accomplishments

## Growth of Conformal Coating by using MLD Technique

- ✓ Coating applied to the laminated electrode, to protect the whole electrode.



- ✓ Conformal coating observed on the particles!
- ✓ The surface exposure to the electrolyte has been protected by the MLD coating.

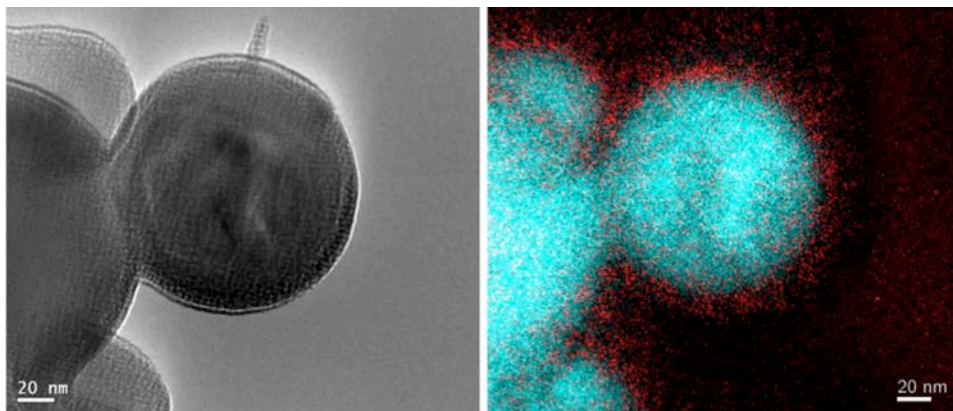


*Adv. Mater.*, 2014, 26: 1596–1601. doi: 10.1002/adma.201304714

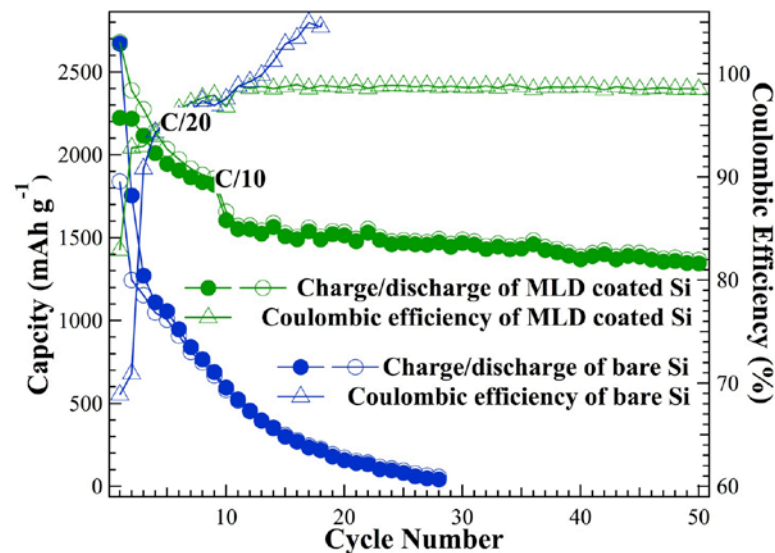
# Technical Accomplishments

## Electrochemical Demonstration of the Alucone Coated Si Anode

- The Si thick electrode ( $\geq 0.8 \text{ mg/cm}^2$ ) is made of Si nanoparticles (50nm, purchased from Alfa), acetylene black (AB) and Polyvinylidene fluoride (PVDF) in a weight ratio of 6:2:2.



EELS elemental mapping (Si – cyan, Al – red) confirming the conformal aluminum alkoxide polymer (alucone) coating on the Si electrode (The growth rate of this MLD reaction is known to be  $2.5 \text{ \AA}$  per cycle at a substrate temperature of  $140^\circ\text{C}$ )



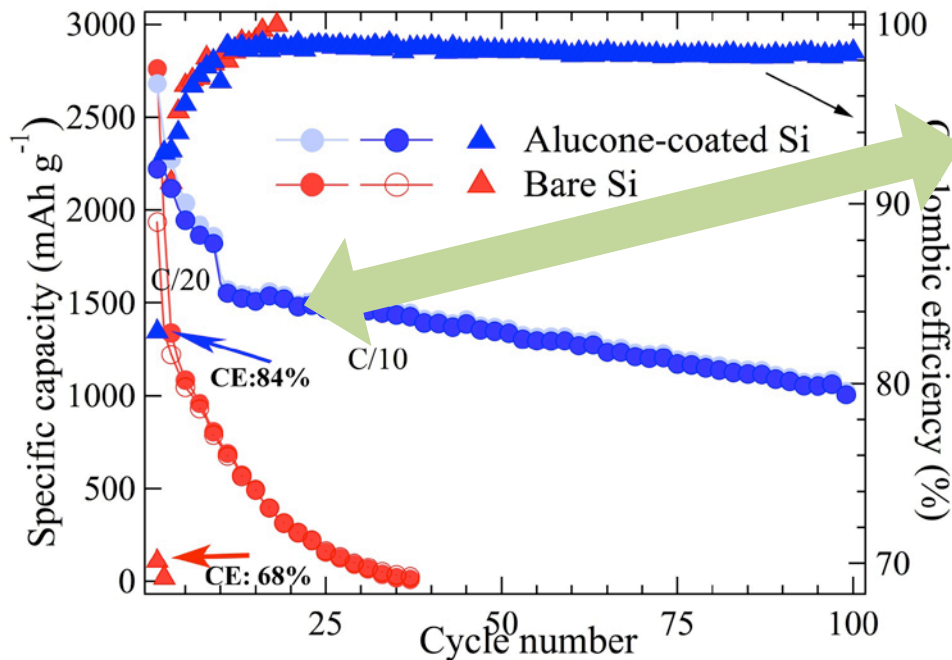
Electrolyte: 1M LiPF<sub>6</sub> in EC/DEC (1:1) without any additives;  
Counter electrode: Lithium metal;  
Voltage window: 0.05V-1V



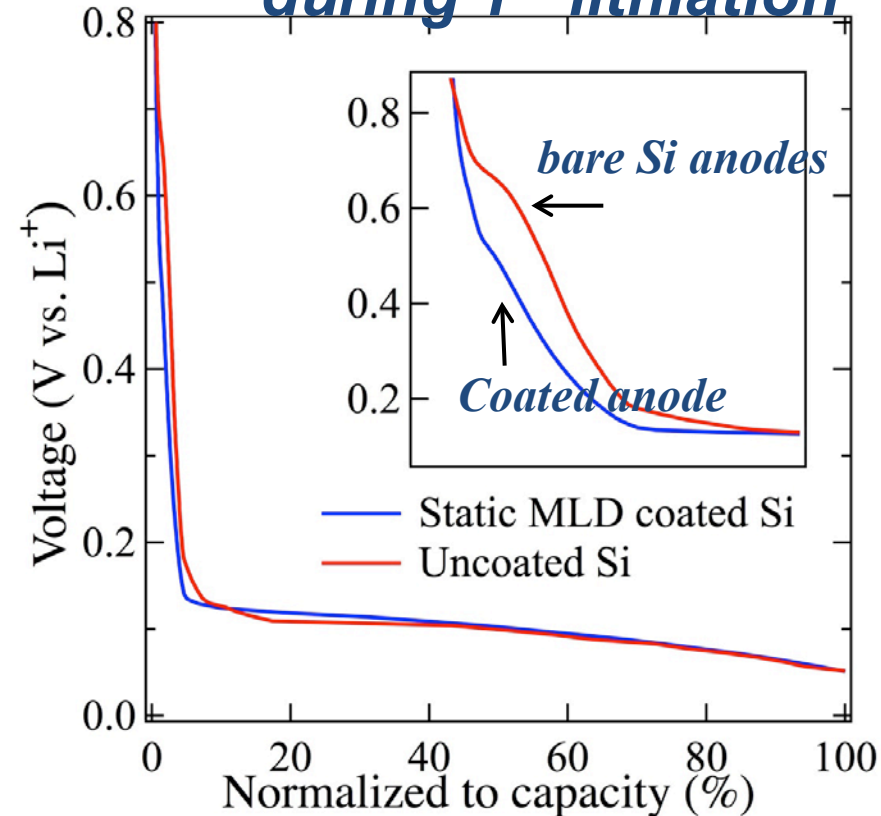
# Technical Accomplishments

## Highly Reversible Capacity Achieved in Alucone coated Si anodes

MLD alucone coating mitigates the inferior interfacial reactions, greatly reduces the irreversible consumption of  $\text{Li}^+$  ions!



### Voltage profile during 1<sup>st</sup> lithiation

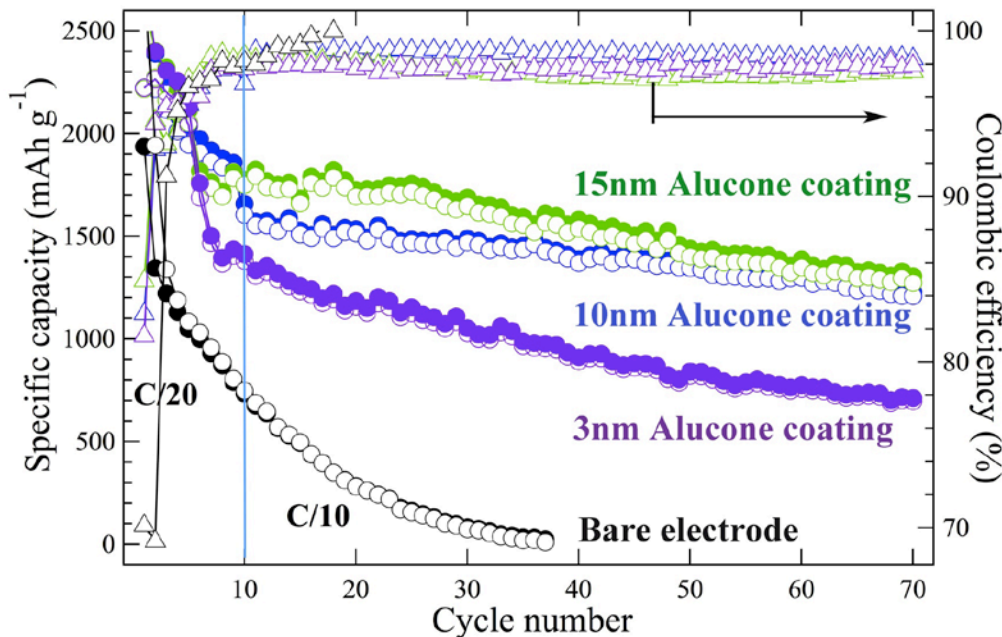
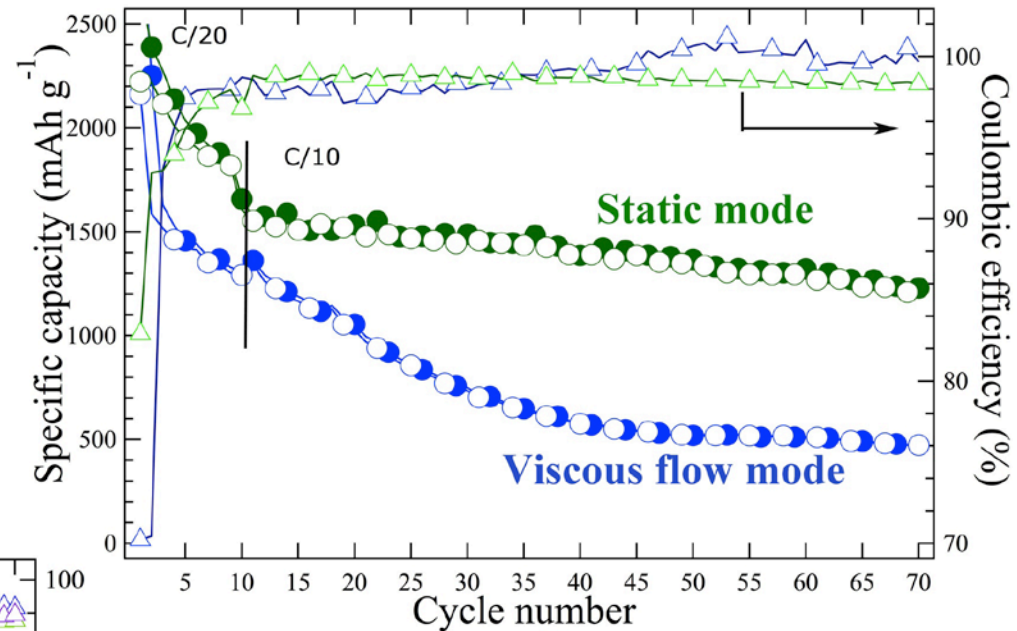


The irreversible capacity at the first cycle drains the lithium from the cathode, thereby sustainable cycling in the full cell requires the higher 1<sup>st</sup> Coulombic efficiency (CE).

# Technical Accomplishments

## Role of Coating Quality on Electrochemical Performance

The static mode is required to obtain the continuous and conformal coating for the porous and tortuous Si electrodes.



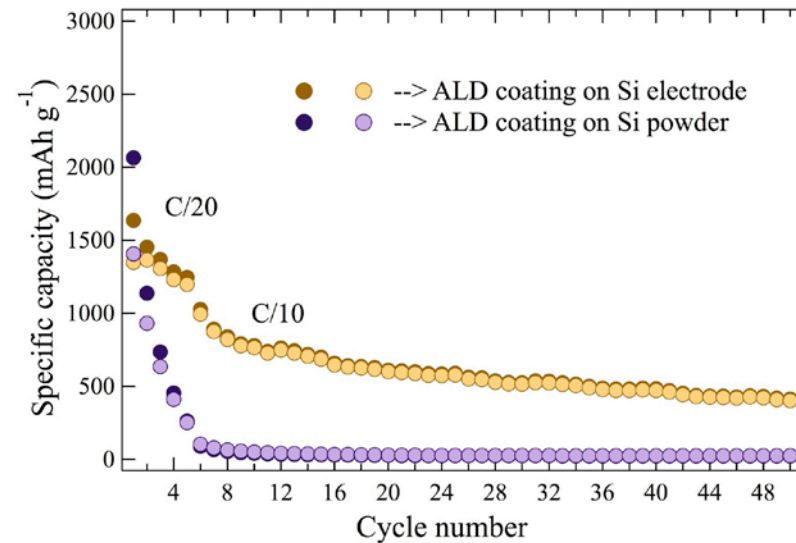
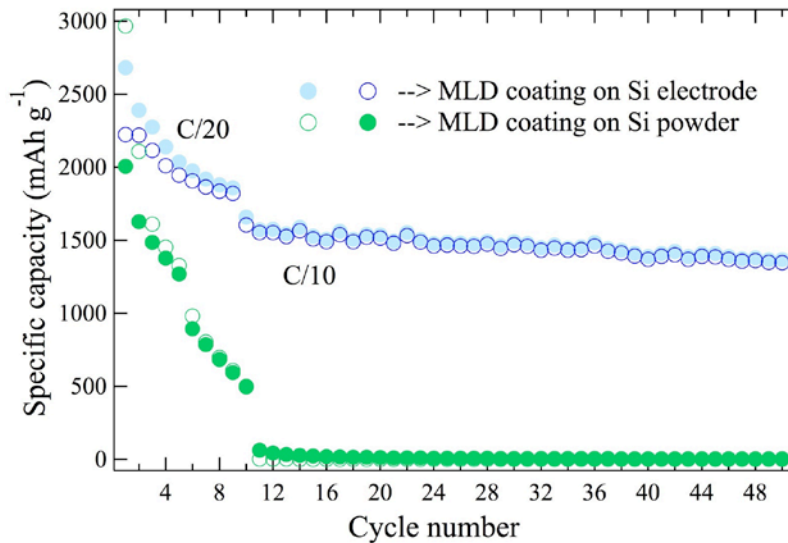
**Coating:** Stabilized cycling performance is obtained in coated anodes; reversible high-capacity is achieved in the thicker coatings (>3nm).

**Cycling conditions:** 175 mA/g (C/20, for the first 5 cycles) 350 mA/g (C/10 for the following cycles)

# Technical Accomplishments

## Improved Cycling Performance Obtained in Coated Electrodes

- Much better cycling performance is achieved when coating the laminated electrodes, because the coated electrode maintains the original electronic path.
- Capacity decay is observed for both electrodes made of ALD/MLD coated Si particles.



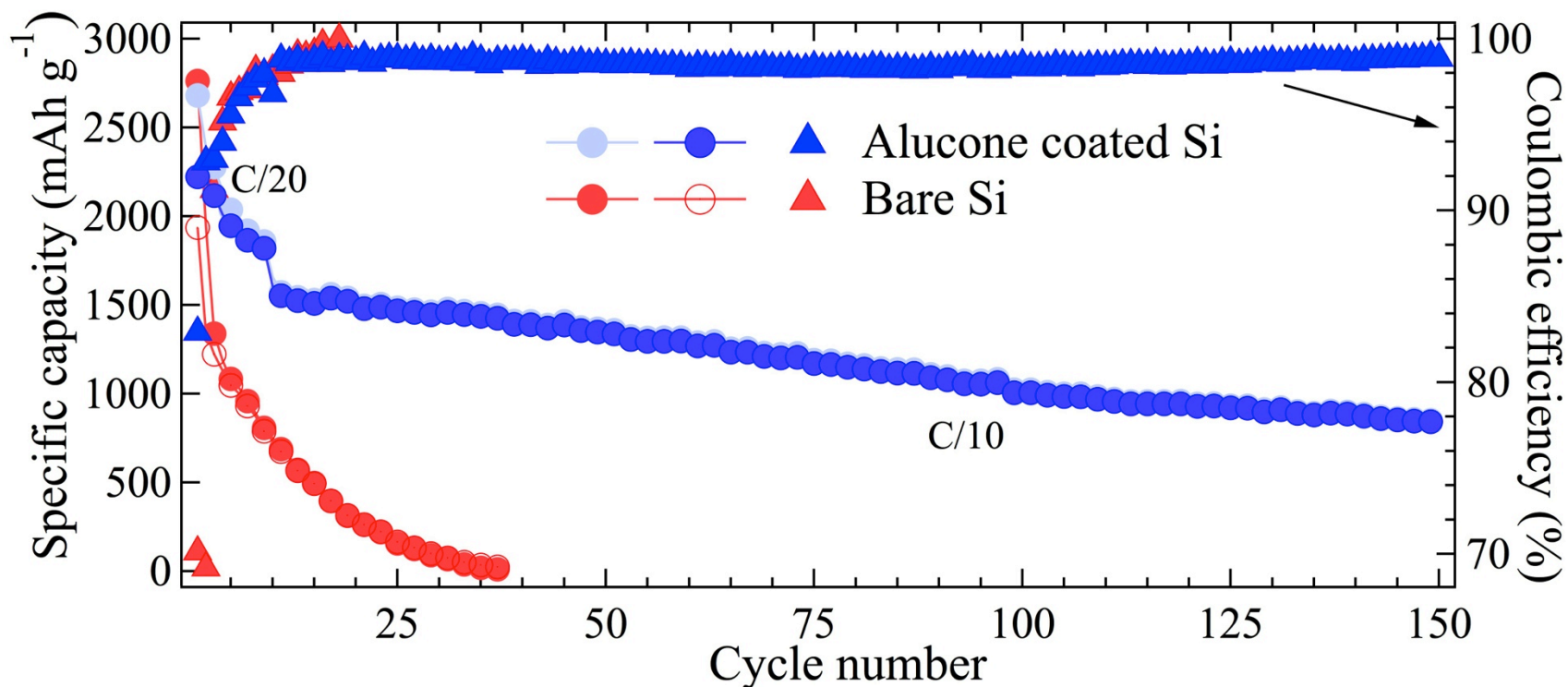
MLD Alucone coating or ALD Al<sub>2</sub>O<sub>3</sub> coating were performed on both Si laminated electrode and Si particles.

- Elastic MLD alucone coating further improves the cycling performance of coated Si anodes, due to the enhanced mechanical properties.

# Technical Accomplishments

## Highly Reversible Capacity Achieved in Alucone-Coated Si Anodes

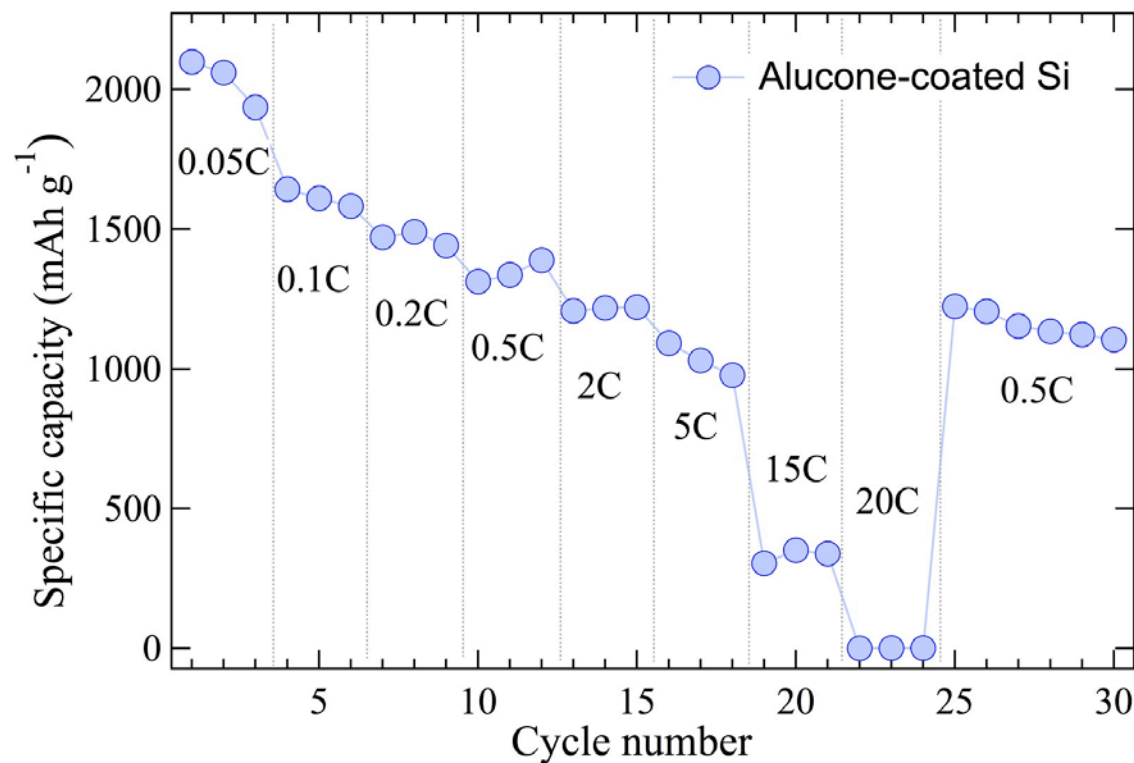
No major capacity fade observed for the MLD-coated Si anode



The coated **Si-C-PVDF** electrodes show sustainable cycling over 100 cycles with capacities of nearly  $900 \text{ mAh g}^{-1}$  ( $0.9 \text{ mAh cm}^{-3}$ ) and Coulombic efficiency in excess of 99%.

# Technical Accomplishments

## Rate Capability Demonstrated in Si Thick Anodes



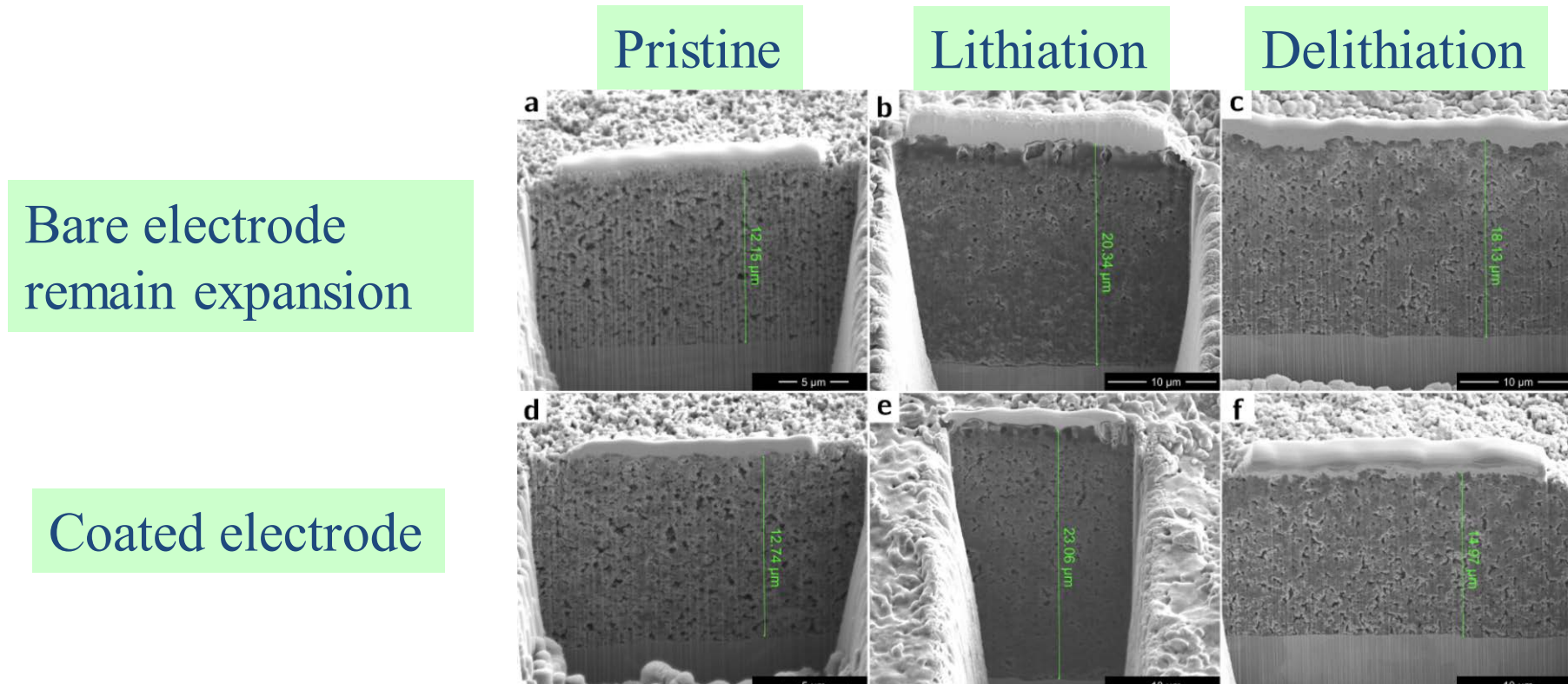
The good resilience of the alucone coatings provides sufficient mechanical support to accommodate the major volumetric changes experienced by Si anodes, *but also enhance the ion transport enabling the rate capability for Si anodes.*



# Technical Accomplishments

## Resilience of the MLD Alucone Coating

- Cross-section SEM images before and after 20 cycles of cycling (volume expansion and contraction) confirm the resilience of the MLD alucone coating;
- Reversible capacity delivered from the repeated volume changes.

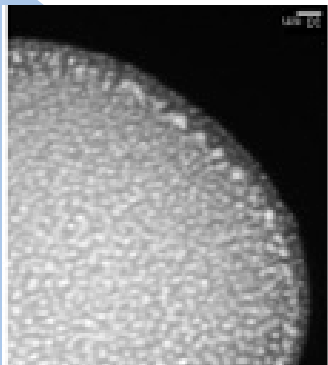


*Repeated volume swelling and shrinking observed in the alucone coated electrode*



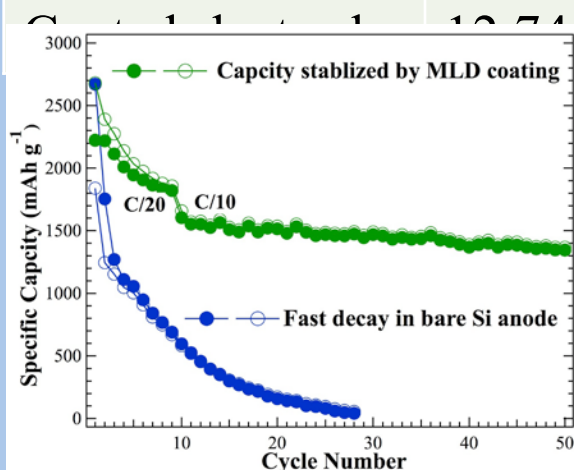
# Technical Accomplishments

## Reversible Cycling of Si Anodes Enabled by Elastic MLD Coating



- ☑ Conformal thin coating of alucone (5nm) accommodates the massive volume expansion and contraction;
- ☑ **A nearly full recovery from the massive volumetric expansion was observed for the alucone coated electrodes;**

| Thickness ( $\mu\text{m}$ ) | Fresh | 1 <sup>st</sup> lithiation | Z-change | 20 <sup>th</sup> delithiation | Z-change |
|-----------------------------|-------|----------------------------|----------|-------------------------------|----------|
| Bare electrode              | 12.15 | 20.34                      | 67%      | 18.13                         | 50%      |
|                             |       | 23.06                      | 81%      | 14.95                         | 17%      |



- ☑ Reversible capacity delivered from the repeated volume changes, thereby excellent cycling performance of coated Si anodes has been achieved by using the alucone coating.

# Technical Accomplishments

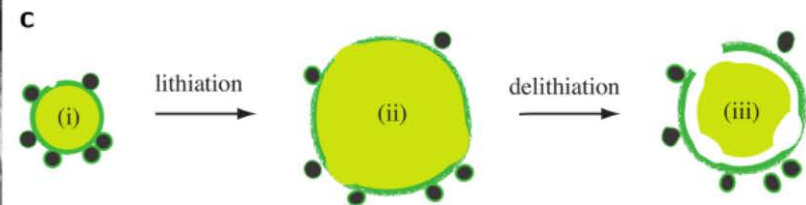
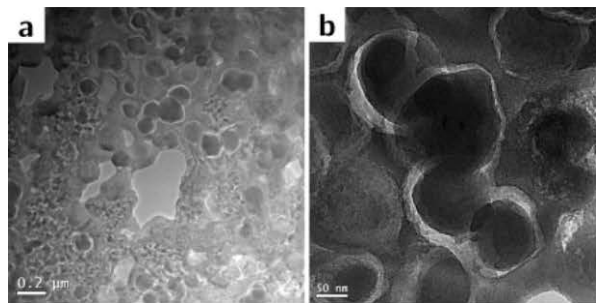
## Great Adhesion Built between Particles and Conductive Network

TEM images of the delithiated Si anodes shown:

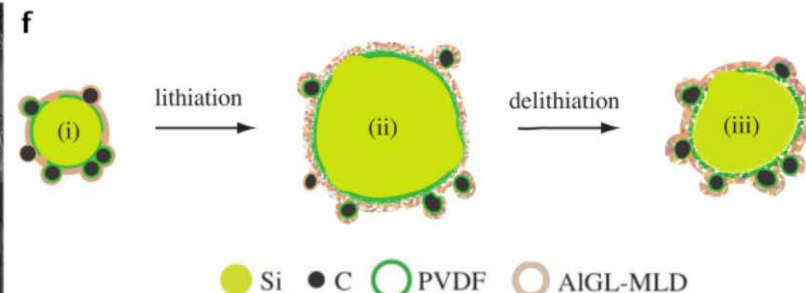
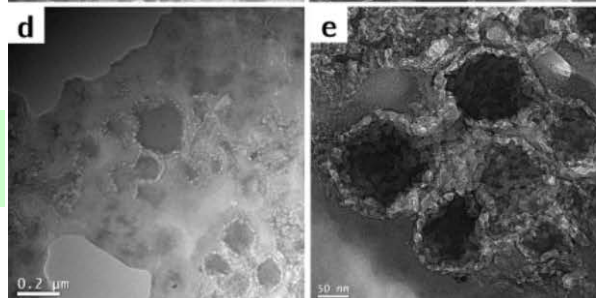
- Bare electrode: severance between particles and the electrode network;
- Coated electrode: intimate adhesion maintained although roughness surface observed after delithiation;

*For the bare electrode, Si particles are isolated from the e/ion conductive network, which results in incomplete reactions in Si particles, finally leads fast decay of cycling capacity.*

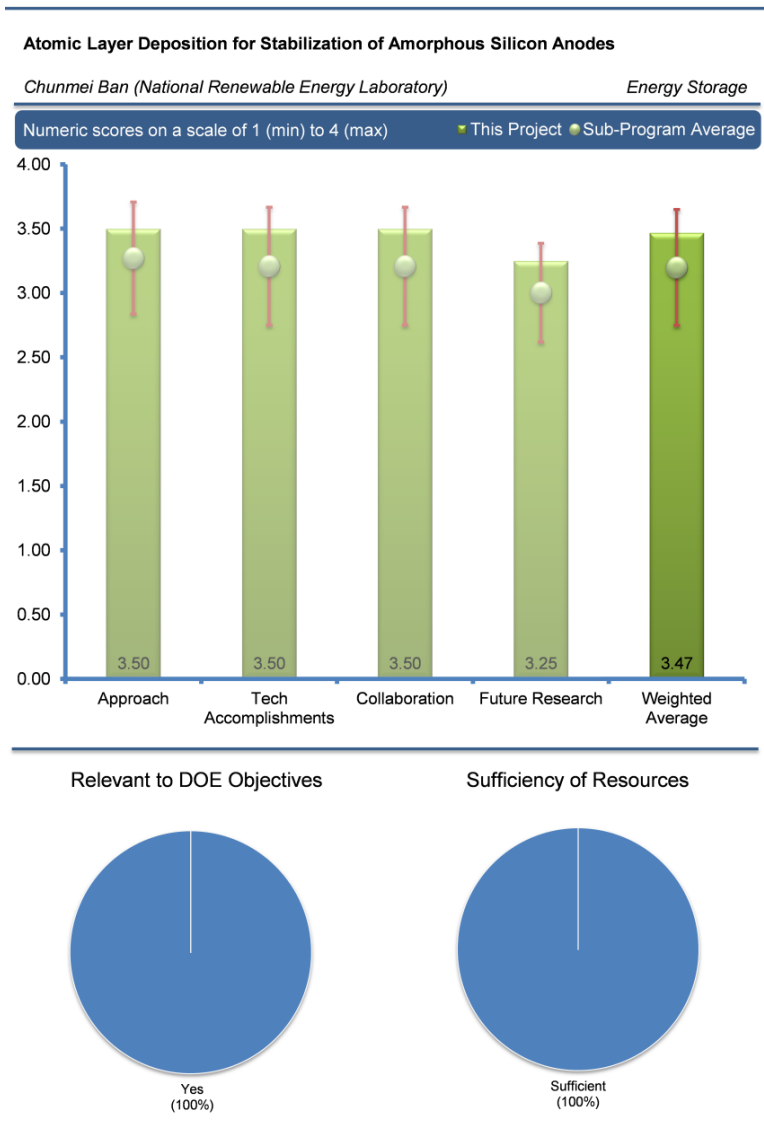
Bare electrode



Coated electrode



# Responses to Previous Year AMR Reviewers' Comments (1/3)



## Approach

- “The reviewer reported that the molecular layer deposition was novel, and a very different approach than others. The approach allowed control over many important parameters and the researchers are doing a great job in leveraging what is known in the literature to make a better SEI into designing their coatings. The reviewer asked if other chemistries would be explored, and how broadly this could be applied to other battery materials”

**Response: Different chemistries have been explored in FY 14 with aiming to improve mechanical integrity and electrochemical performance.**

- “The reviewer concluded that the resultant material should be both electronically and ionically conductive and mechanically strong.”
- “The reviewer felt the program had an innovative approach to control Si anode swelling at the electrode level.”

**Response: Improved conductivity is expected when introducing carbon domain and aromatic rings into the coating chemistry.**

# Responses to Previous Year AMR Reviewers' Comments (2/3)

## Technical achievements

- *“The reviewer saw that good progress had been made this past year. The investigators have developed a technique that improved the stability of a Si anode by an aluminum alkoxide polymer coating, and also demonstrated improved performance of a Si-polyacrylonitrile (PAN) composite anode.”*
- *“The reviewer reported that the milestones were very quantitative and that the researchers were hitting them. In addition, there were good hypotheses, and data to support/refute those hypotheses. The characterization was very appropriate and supported the approach. The reviewer would like to see some other performance targets such as power in the future. .”*

***Response: Greatly improved rate capability has been demonstrated by using MLD alucone coating, as elaborated in recently published paper (Adv. Mater., 2014, 26: 1596–1601. doi: 10.1002/adma.201304714).***

- *“The reviewer felt the performance results of MLD coated Si anode was more promising than that of Si-PAN composite, and recommended that future efforts focus on the MLD approach.”*  
*“The reviewer stated that although ALD is a good approach, cost effective issues have to be addressed for practical applications.”*

***Response: In FY14, the research is focusing on MLD approach. MLD alucone coating has been developed to significantly improved both energy and power capability for Si anodes.***

***New coating conditions for ALD/MLD is being developed in order to coat electrodes more efficiently and work at atmospheric pressure, which will greatly reduce cost.***

## Responses to Previous Year AMR Reviewers' Comments (3/3)

**Collaboration:** *“The reviewer reported there was a broad range of collaborators, and thought that it was also nice to see this type of approach being applied to cathodes (see interaction with Burrell/ANL on Li-rich materials).”*

**Response:** *Great collaboration work with Burrell/ANL has been made in FY14 to address coating effect for Li-rich materials, which is published in J. Power Sources, 2013, doi.org/10.1016/j.jpowsour.2013.10.035.*

**Future Work:** *“The reviewer thought that the approach looked promising enough that more work on scale-ability and practical implementation should be addressed.”*

*“The reviewer reported that the proposed future plans were good, but again warned that cost issues have to be addressed.”*

*“The reviewer felt that the researchers needed to demonstrate that the project can achieve similar good cycle life on a thicker Si anode (i.e., more loading) and also with a thinner MLD coating that does not compromise rate capability.”*

**Response:** *The research in FY 14 is focusing on different chemistries in MLD coating to address both high-capacity and high-power capabilities.*

*Furthermore, the working with Dr. Tenent/ABR project is continued to develop in-line ALD and roll-to-roll ALD process at atmospheric pressure, to address the scale-ability and practical implementation.*

*All of Si electrodes in this research are made of commercial Si particles with AB and PVDF in 6:2:2 wt. ratio, having a high mass loading  $\geq 0.8 \text{ mg/cm}^2$ .*

# Collaborations

**Collaborations with Universities and National labs have been built to investigate the coating effects on the Si anodes and Li-rich cathodes**

*Lawrence Berkeley National Laboratory (LBNL):*

Dr. Phil Ross: FTIR, XPS to study SEI formation

Dr. Rob Kostecki: near-field IR for coating effect on Si singlecrystal anodes

Dr. Gao Liu: Coating effect on the thin and thick Si anodes

*Pacific Northwest National Lab (PNNL):* Dr. Ji-Guang Zhang and Dr. Chongming Wang: In-situ morphology characterization

*Texas A&M University:* Prof. Perla B Balbuena: theoretical simulation of the coating chemistry and stability

*Sandia National Lab (SNL):* Dr. Kevin Leung: theoretical simulation of the structure and diffusion mechanism

*Michigan State University and GM Research:* Prof. Yue Qi and Dr. Xingcheng Xiao: Theoretical and experimental research on mechanical properties

*Stanford University:* Prof. Yi Cui: Identify the structure/morphology evolution on the coated Si nanowires.

*Argonne National Lab (ANL):* Dr. Anthony Burrell and Ira Bloom on high-voltage Li-excess cathode materials to identify the effect of coating on voltage fading.



# Future Plans

- ❑ Demonstrate durable cycling performance of thick Si anodes ( $>15\mu\text{m}$ ) by using new MLD coatings;
  - Develop conductive and mechanically strong coating by using MLD;
  - Establish the optimal composition and structure of the MLD coatings to improve the surface stability of Si particles and to increase the integrity of Si electrodes;
- ❑ Explore the importance and mechanism of various coatings via the BATT coating group;
  - Perform characterization and analyses to better understand the structural evolution of coated electrodes during cycling; Investigate the effect of coating on the formation of solid electrolyte interphase (SEI) to reduce the irreversible capacity loss due to inferior SEI reactions;
  - Identify the ionic diffusion and mechanical properties of the MLD coatings using theoretical simulation;
- ❑ Collaborate within the BATT program with the aim of developing high-rate plug-in hybrid electric (PHEV) compatible electrodes.
  - Demonstrate the optimized coating chemistry to enable Si anodes having high-durable capacity and high-rate capability in a full cell.

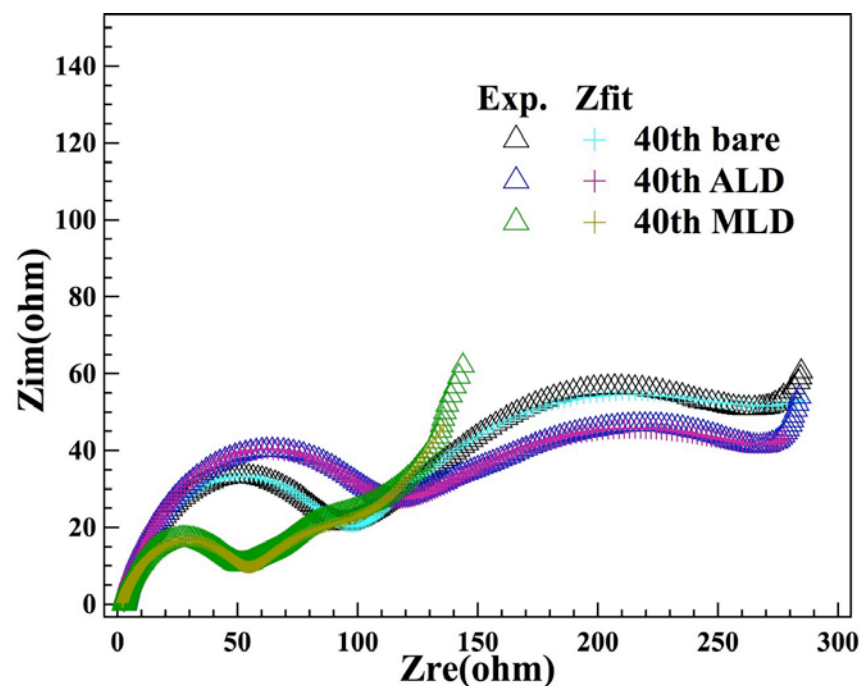
# Summary

- ✓ Developed conform MLD alucone coating on porous electrodes by using sequential and self-limited MLD reaction between trimethylaluminium and glycerol precursors.
  - **Significantly improved** the cycling performance of conventional Si-C-PVDF electrodes. The capacity has been stabilized in the MLD-coated Si electrode.
  - **No major capacity fade** observed after 150 charge-discharge cycles, and the Coulombic efficiency reaches ~99% in the MLD-coated Si electrode.
  - **Rate-capability** demonstrated for the alucone coated Si anodes
- ✓ Achieved highly reversible capacity in alucone coated Si anodes with greatly improved 1<sup>st</sup> cycle Coulombic efficiency (from ~65% in bare Si anodes to 85% in coated Si electrodes);
- ✓ Observed a nearly full recovery from the massive volumetric expansion for the alucone coated electrodes, thereby the elastic coating enabling Si anodes reversible cycling.

# Technical Back-up Slides

# Enhanced Conductivity Achieved in MLD Alucone Coatings

- Alucone coating synthesized by MLD chemistry shows improved ionic conductivity, therefore, rate performance has been achieved for the MLD coated Si electrodes.



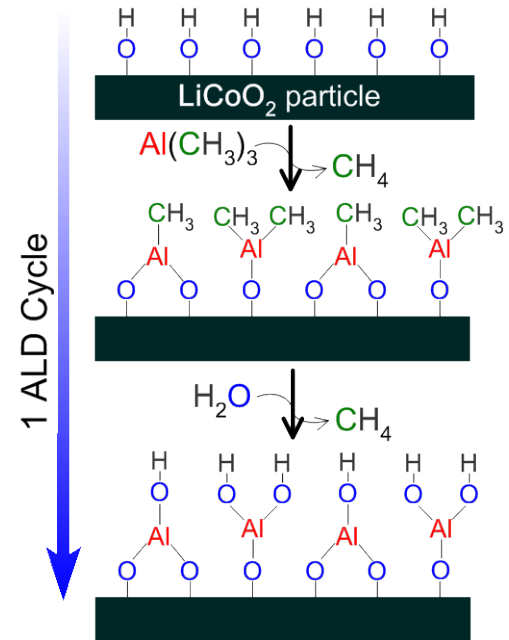
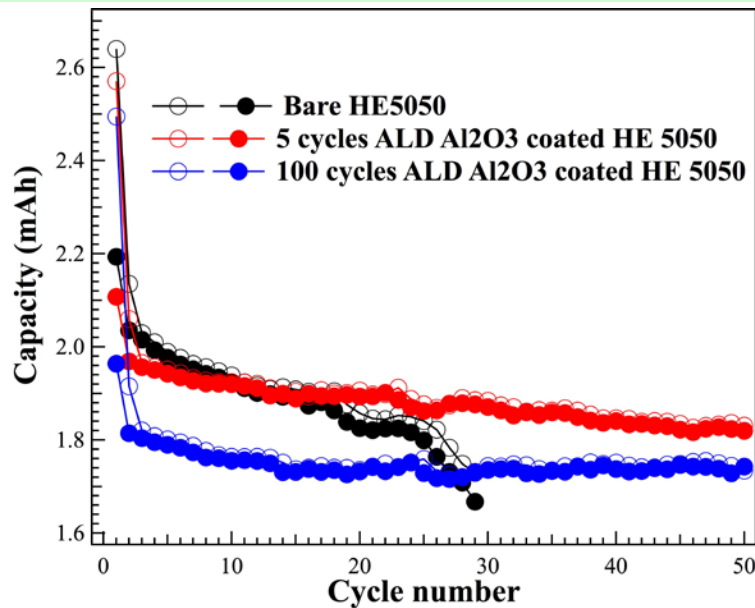
EIS spectra (experimental and Zfit data) of bare, ALD coated and MLD coated carbon electrodes after the 40<sup>th</sup> cycles.

- Electrochemical impedance data (left) show that the decreased resistance in the SEI layer upon the stabilization of this natural surface layer formation throughout cycling progression;
- The lowest resistance in both SEI layer and charge transfer reactions observed from the MLD coated electrode;
- The drastic increment in the resistance observed for the bare electrode.

# Enhanced Conductivity Achieved in MLD Alucone Coatings

ALD  $\text{Al}_2\text{O}_3$  coatings with different thickness have been applied to Li-rich cathodes.

Sustainable cycling performance has been achieved in ALD coated electrodes.



- Figure exhibits the improved cycling performance of high-capacity Li-rich electrodes after ALD coating;
- Lower capacity observed for thick ALD coating due to the electronically insulating coating.