Conformal Corrosion-Resistant Coatings for Fuel Cell Bipolar Plates by Atomic Layer Deposition

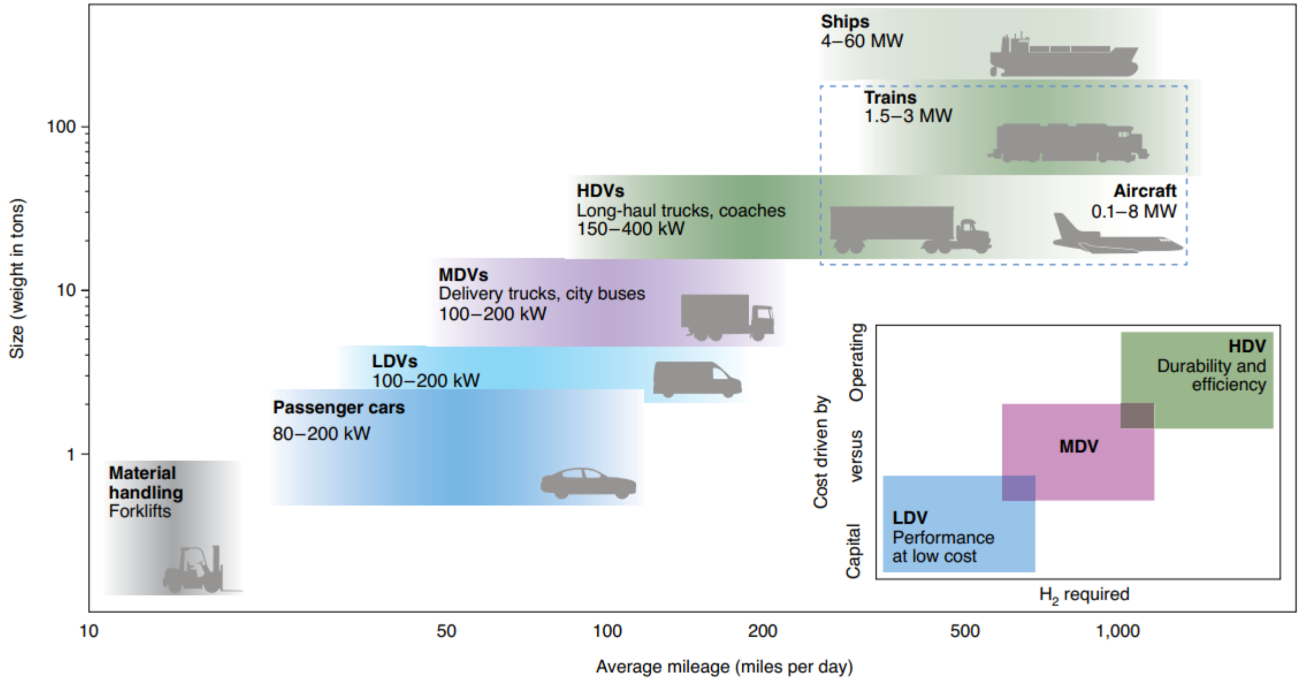
Katherine Hansen
Radiation Monitoring Devices (RMD Inc.)

DE-SC0023931
05/08/24

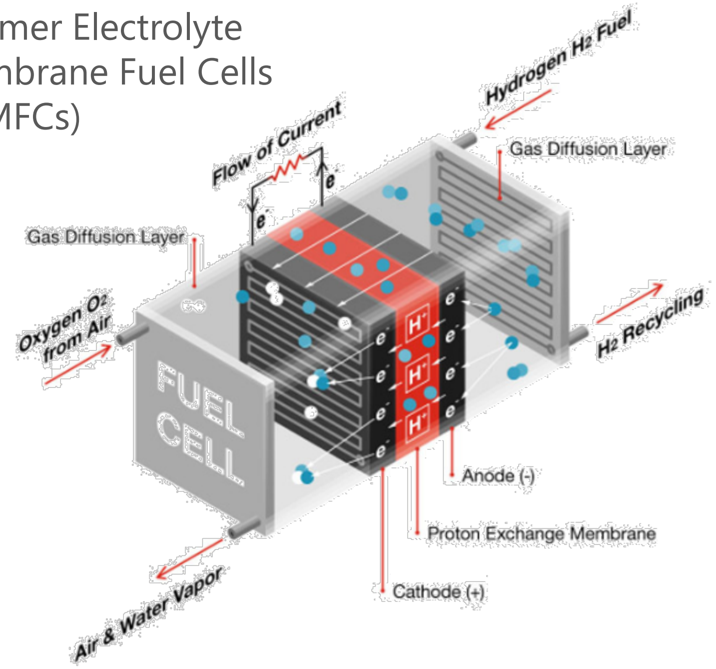
DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

AMR Project ID #
MNF-BIL016

Project Goal



Polymer Electrolyte Membrane Fuel Cells (PEMFCs)



- Outlook: Develop robust protective coating to prevent corrosion and extend the lifetime of bipolar plates (BBPs) while maintaining the necessary electrical conductivity and mechanical strength
- Challenge: A highly conductive, pin-hole free coating with good adhesion to the complex flow fields of stainless steel BBPs

Cullen, D. A., Neyerlin, K. C., Ahluwalia, R. K., Mukundan, R., More, K. L., Borup, R. L., ... & Kusoglu, A. (2021). New roads and challenges for fuel cells in heavy-duty transportation. Nature energy, 6(5), 462-474.
https://www.cummins.com/news/2019/10/08/five-key-questions-about-next-frontier-hydrogen-fuel-cells

Overview

Timeline and Budget

- Project Start Date: 07/10/2023
- Project End Date: 04/09/2024

- Total Project Budget: $199,981
  - Total DOE Share: $199,981
  - Total Cost Share: $0
  - Total DOE Funds Spent*: $82,750.72
  - Total Cost Share Funds Spent*: $0

    * As of 03/01/2024

Partners

- **Cummins:** Subcontractor

Barriers and Targets

- **Problem:** Thin, metallic BPPs are susceptible to corrosion in the PEMFC environment
- **Outlook:** Develop robust protective coating to prevent corrosion and extend the lifetime while maintaining the necessary electrical conductivity and mechanical strength of BPPs
- **Challenge:** A highly conductive, pin-hole free coating with good adhesion to the complex flow fields of stainless steel BBPs
- **Solution:** Conformal atomic layer deposition (ALD) coating of conductive metal nitride film that is pin-hole free

Relevance to DOE Goals

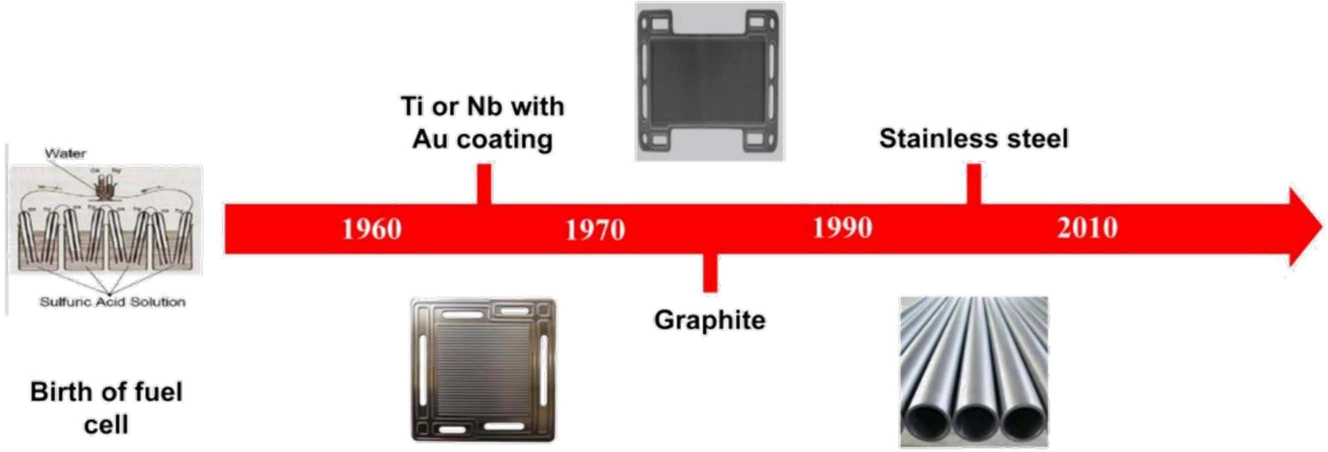
DOE Targets

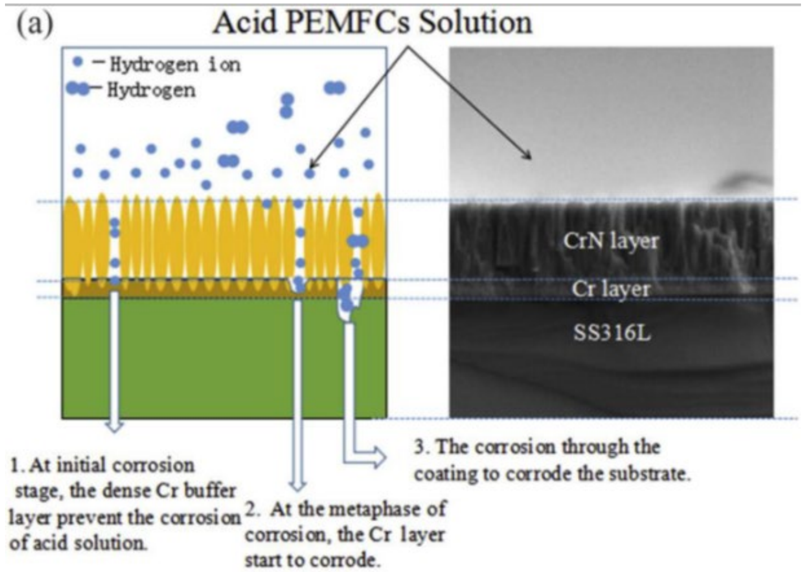
- Renewable hydrogen as an energy source to meet the energy needs of heavy-duty vehicles (HDVs), Million Mile Fuel Cell Truck Consortium (M2FCT) to reduce emissions
- Near-term target (2027) for HD fuel cell manufacturing capacity
  - 20,000 PEMFC stacks/year
  - Production rate of 2400 BPPs per hour

BPP Functions	Characteristic	Units	Target
Connect cells electrically one by one; conduct electrical current	Electrical conductivity	Scm^{-1}	>100
	Areal specific resistance	Ωcm^2	<0.01
Separate the reaction gases	H_2 permeability	$cm^3 sec^{-1} cm^{-2}$	2×10^{-6}
Facilitate heat management	Thermal conductivity	$Wm^{-1}K^{-1}$	/
Durability	Corrosion, anode	μAcm^{-2}	<1 and no active peak
	Corrosion, cathode	μAcm^{-2}	<1
	Lifespan	hours	8000
Light weight	Plate weight	kg/kW	0.18
Economy	Cost	$\$kW^{-1}$	2
Good mechanical properties	Flexural strength	MPa	>40

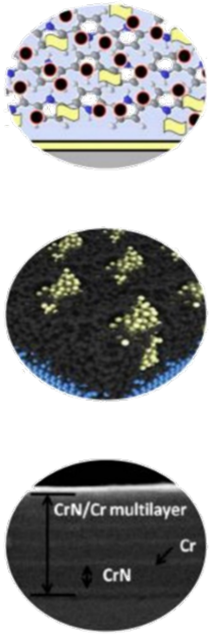
Papageorgopoulos, D. (2023). Fuel Cell Technologies Overview. Department of Energy, Arlington VA. https://www.hydrogen.energy.gov/docs/hydrogenprogramlibraries/pdfs/review23/fc000_papageorgopoulos_2023_o.pdf
DRIVE, U. (2017). Fuel Cell Technical Team Roadmap, 45-59. Department of Energy, USAFarrington, S. Manufacuting Issues in Bipolar Plate Production, https://stage.energy.gov/sites/default/files/2017/05/f34/fcto_biploar_plates_wkshp_farrington.pdf.

Potential Impact





- State-of-the-art BPP coatings still allow for corrosion through pinholes and grain boundaries
- Need conductive, pin-hole free coating with good adhesion to the complex flow fields of SS BBPs



Coated stainless steel

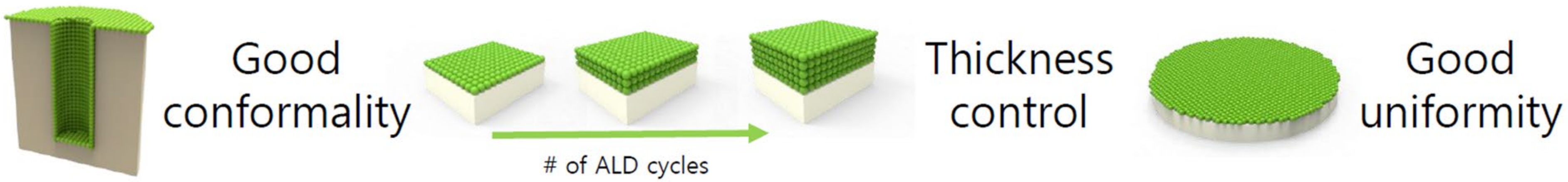
Stainless Steel (SS) BPPs Advantages

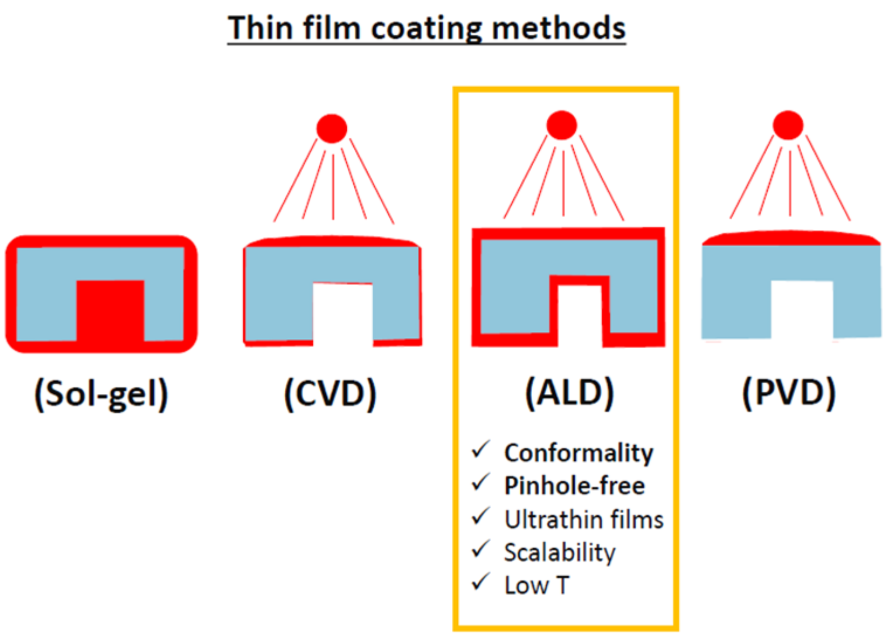
- High strength allowing thinner plates for high power density
- High bulk electrical and thermal conductivities
- Potential for low cost
- Existing low cost/high volume manufacturing
- However, can corrode in PEMFC operation

Liu, R., Jia, Q., Zhang, B., Lai, Z., & Chen, L. (2022). Protective coatings for metal bipolar plates of fuel cells: a review. International Journal of Hydrogen Energy, 47(54), 22915-22937.

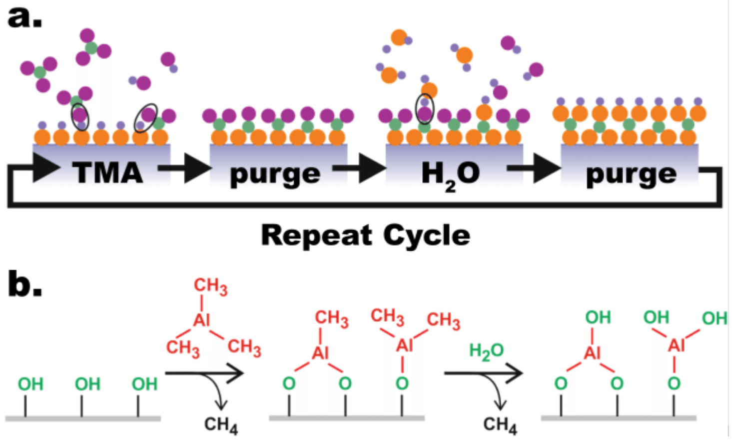
Approach

Atomic Layer Deposition (ALD)





- ALD is driven by surface chemistry to provide conformal coatings on complex flow fields in BPPs
- ALD provides, uniform, pin-hole free coatings
- ALD has high yield/batch for scaling up and low-cost production



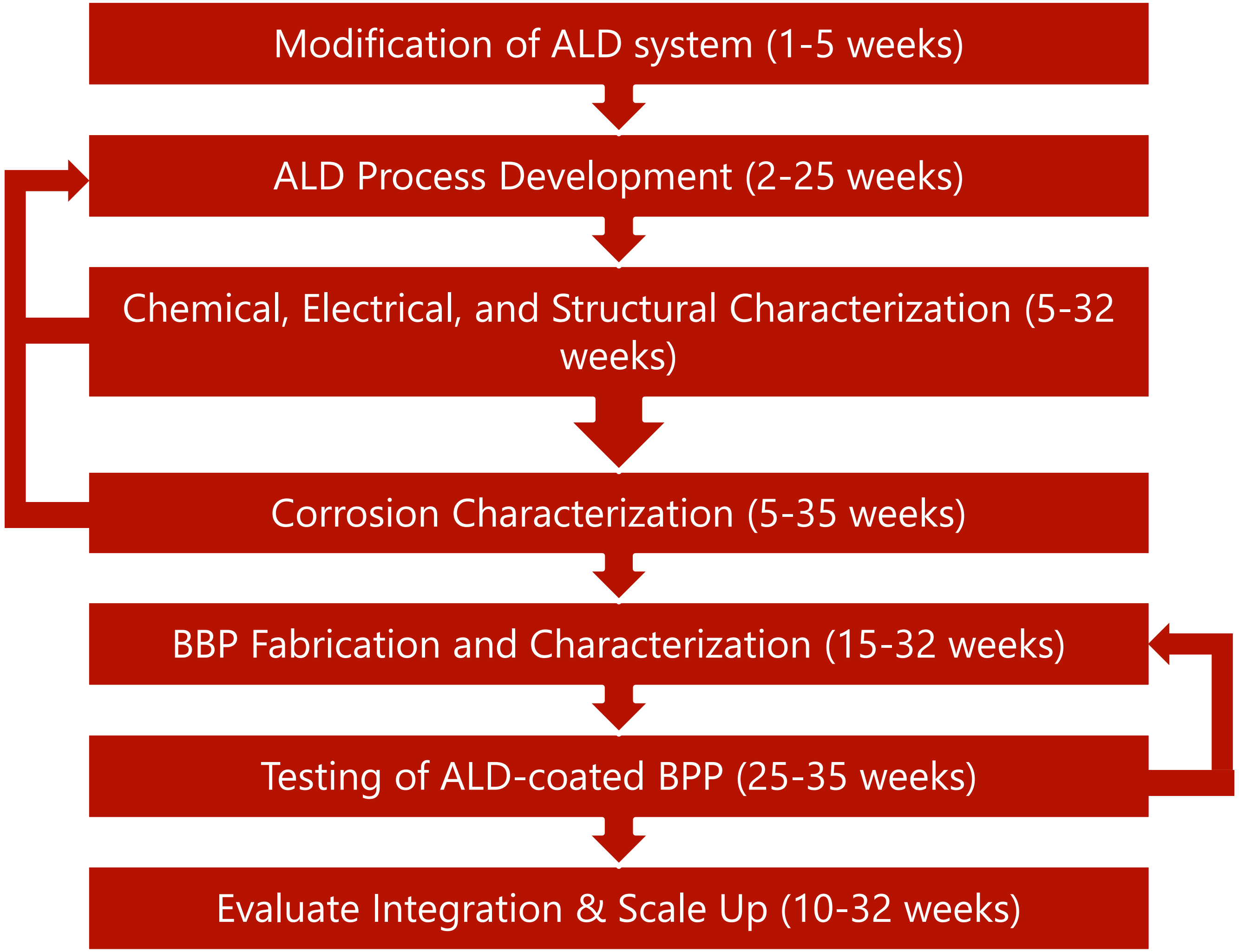
Grillo, F., Moulijn, J. A., Kreutzer, M. T., & van Ommen, J. R. (2018). Nanoparticle sintering in atomic layer deposition of supported catalysts: Kinetic modeling of the size distribution. *Catalysis Today*, *316*, 51-61.
Karimzadeh, S., Safaei, B., Yuan, C., & Jen, T. C. (2023). Emerging atomic layer deposition for the development of high-performance lithium-ion batteries. *Electrochemical Energy Reviews*, *6*(1), 24.

Approach Cont.

Technical Objectives

1. Demonstrate the durability of a conductive, protective coating via ALD
    a. Demonstrate electrical conductivity >100 S/cm
    b. Demonstrate corrosion at the anode <1 $\mu A/cm^2$ with no active peak,
    c. Demonstrate corrosion at the cathode <1 $\mu A/cm^2$

2. Evaluate and validate the performance of ALD-coated BPP by performing tests on a fuel cell test stand comparing performance against an uncoated BBP



Approach Cont.

Testing to Perform	Methods	Phase 1	Phase 2
Coating Corrosion Resistance	Galvanostatic Operation in 3-electrode cell	At RMD	At RMD
Coating Electrical Conductivity	4-Point Probe	At RMD	-
Coating Thermal Conductivity	Thermal Conductivity Analyzer	At Cummins	-
Coating Surface Morphology	Scanning Electron Microscope	At RMD	At Cummins
Coating Elemental Composition	X-Ray Analyzer	At RMD	At Cummins
Chemical Stability	Aging Chamber (stress in chemical environment)	-	At Cummins
Thermal Stability	Aging Chamber (stress at high temperature and humidity)	-	At Cummins
Mechanical Stability	Aging Chamber (stress under compressive load)	-	At Cummins
Bond Strength (Delamination)	Instron Mechanical Tester	At Cummins	-
Contact Angle (Water Management)	Surface Energy Analyzer	At Cummins	-
Flexural Strength	Instron Mechanical Tester	At Cummins	-
Thickness Uniformity	Professional Caliper	At Cummins	-
Accuracy of flow field dimensions (they must be within tolerance)	Keyence Optical Microscope	At Cummins	-
Performance Test (Voltage vs Current)	Fuel Cell Test Stand	At Cummins	At Cummins

Approach: Safety and Planning Culture

- This project was not required to submit a safety plan for review by the HSP.

Prioritizing Safety/Analyzing Hazards

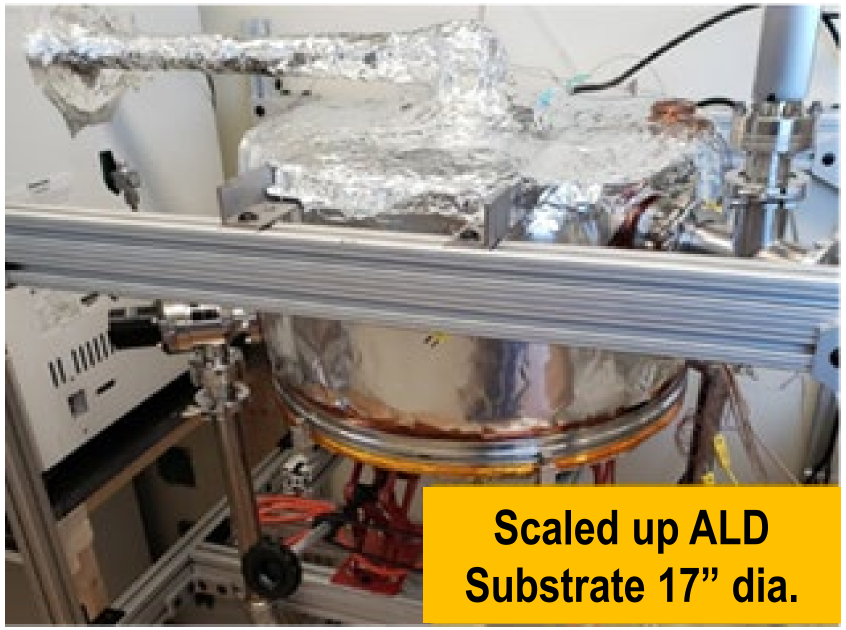
- RMD has a Chemical Safety Team that oversees all safety planning and helps establish safety practices that are available to all employees
- Plan on conducting HAZOP for system operation

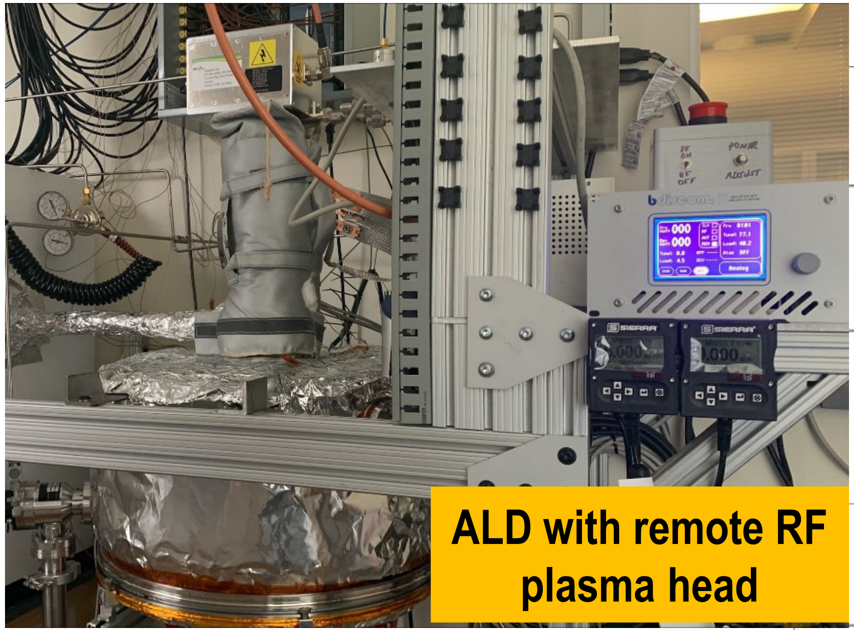
Best Practices/Lessons Learned

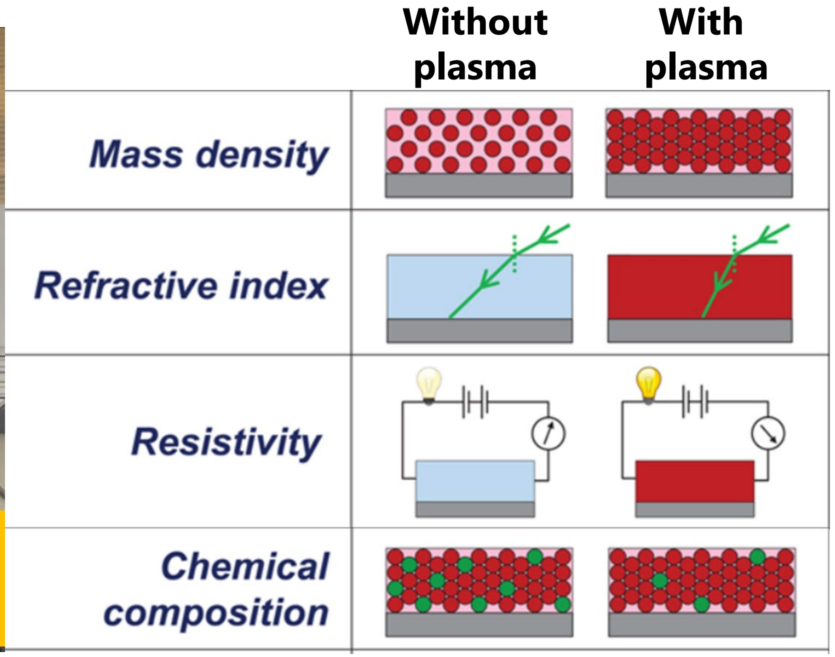
- All team members have been trained on the system for reporting safety concerns
- Regular meetings include all team members and address issues impacting safety concerns

Accomplishments and Progress

Upgraded ALD System





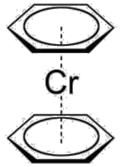


- Installed remote RF plasma system from Meaglow Ltd.
- Plasma-enhanced ALD (PEALD) expands properties and application of ALD tailoring material properties while maintaining low processing temperatures

Faraz, T., Knoops, H. C., Verheijen, M. A., Van Helvoirt, C. A., Karwal, S., Sharma, A., ... & Kessels, W. M. (2018). Tuning material properties of oxides and nitrides by substrate biasing during plasma-enhanced atomic layer deposition on planar and 3D substrate topographies. *ACS applied materials & interfaces*, *10*(15), 13158-13180.

Accomplishments and Progress Cont.

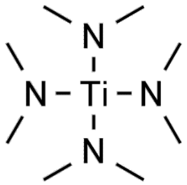
CrN

- No ALD literature
- CVD
  -  + NH_3/N_2H_4

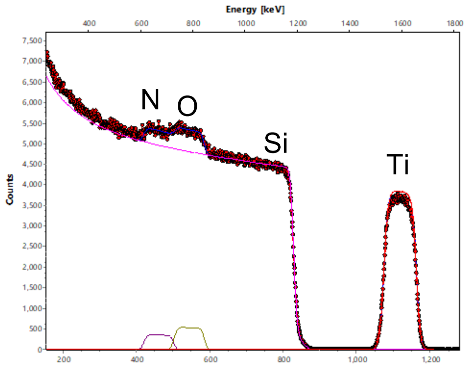
  - 400°C amorphous, dense and smooth
  - 67 kJ/mol
- Attempt ALD, but Cr precursor not volatile enough
- As alternative, investigate sputter deposition of Cr then nitridation to CrN via NH_3 plasma in ALD system

TiN

- RMD grows by ALD
- Thermal ALD
  - TDMAT + NH_3
    - 9.7 kJ/mol
  - TDMAT + N_2H_4
    - -14.4 kJ/mol

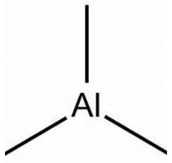


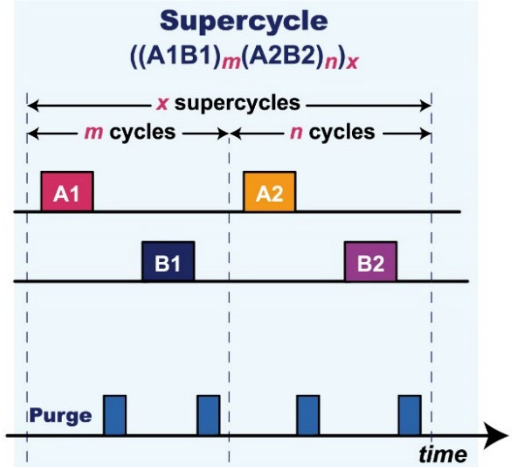
- Plasma Enhanced ALD
  - With new plasma ALD system using NH_3 plasma
    - Films are TiON, by RBS



TiAlN

- Can grow with supercycle of TiN and AlN
- TiN established
- AlN in literature
  - TMA + NH_3
    - -119/8 kJ/mol
  - TMA + NH_3 (plasma) reported



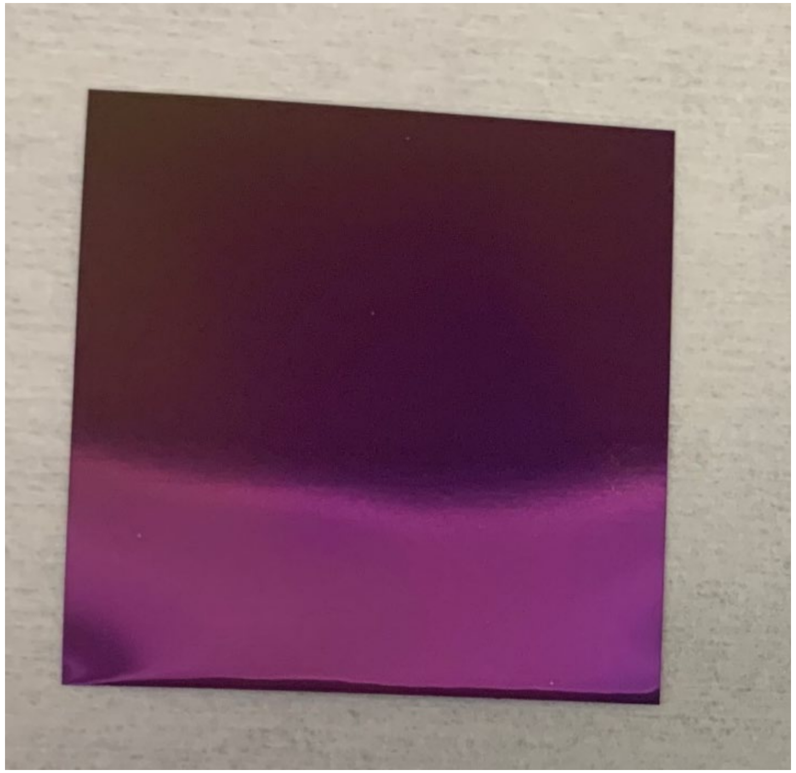


Faraz, T., Roozeboom, F., Knoops, H. C. M., & Kessels, W. M. M. (2015). Atomic layer etching: What can we learn from atomic layer deposition?. *ECS Journal of Solid State Science and Technology*, *4*(6), N5023.

Accomplishments and Progress Cont.

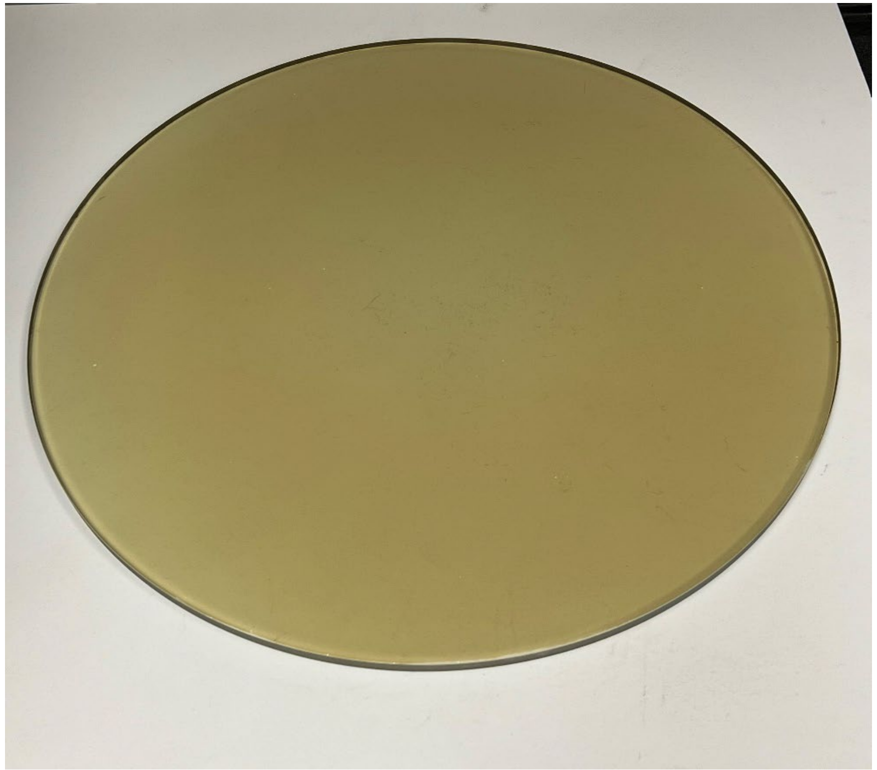
25 nm ALD TiN film on a 16” diameter ceramic disk

Conductivity ~13.9 x10^6 S/cm



130 nm PEALD TiN film on a 2” x 2” 316L SS coupon

Conductivity ~4294 S/cm



40 nm PEALD TiN film on a 17” diameter glass window

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This project was not reviewed last year

Collaboration and Coordination

- U.S. DOE – Project Sponsor
- RMD Inc. – Prime/Project Manager
- Cummins Inc. – Subcontractor

DEIA/Community Benefits Plans and Activities

RMD's Core Values

- **INTEGRITY:** We act with integrity and honesty in accordance with the highest professional, and ethical standards.
- **RESPECT:** We respect and honor the dignity of each person and foster a diverse and inclusive work environment.
- **RESPONSIBILITY:** We act responsibly, and we are accountable for our decisions, actions, and their consequences.
- **DISCOVERY:** We seek and create new knowledge and understanding, and foster creativity and innovation, for the benefit of our communities, society, and the environment.
- **EXCELLENCE:** We strive for excellence in all our endeavors both as individuals, and as a company.

RMD's Specific Goals

- Increase recruitment, hiring, retention, and the success of female and underserved staff. Our goal is to make sure that a minimum of 25 percent of the new hires at RMD are either female or from an underserved community.
- Institute policies and practices that ensure equity for underserved minority, and other diverse staff.

RMD's Activities

- Promoted a female Team Leader to Director
- In the past year 40% of positions were filled by females and underserved community members
- 7 out of 12 interns and co-op students over the past two years were females and underserved community members

Remaining Challenges and Barriers

Challenge/Barrier	Solution
CrN ALD – precursor volatility is not sufficient in current setup	• As alternative, investigating sputter deposition of Cr then nitridation of it into CrN via NH_3 plasma in the ALD system • In future can employ direct liquid injection for higher volatility and ALD growth of CrN
Discovered oxygen in films indicating leak in ALD system	• Determine source of leak and address it, unfortunately out of scope for the Phase I of this project and unlikely timeline wise • Evaluate current oxynitride films knowing nitride films should perform even better
Issues with Electrochemical Corrosion Testing	• RMD's setup for electrochemical corrosion testing was determined to be insufficient for required testing and thus could not be performed reliably to screen candidate coatings • Cummins instead will perform some coupon corrosion testing

Proposed Future Work

In Rest of Phase I Period (FY24)

- Evaluation of candidate coatings by Cummins
- Coating and evaluation of BPP on test stand at Cummins
- Evaluate ALD scale-up and perform cost estimate analysis
- Engage DOE and PEMFC technology experts on results of this work

In Potential Phase II Period (FY25)

- Continue evaluating BPP performance with coating on test stands
- Investigate appropriate surface cleaning of BBPs for refurbishment
- Work with PEMFC manufacturers to bring this coating and refurbishment technology to their process

Summary

- DOE goal in M2FCT is for renewable hydrogen to be utilized as an energy source to meet the energy needs of HDVs to reduce emissions
- PEMFC are promising for this goal, however the SS BPPs are susceptible to corrosion
- Need to develop robust protective coating to prevent corrosion and extend the lifetime while maintaining the necessary electrical conductivity and mechanical strength of BPPs
- This project aims to utilize conformal ALD coatings of conductive metal nitride film that are pin-hole free as highly conductive corrosion-resistant coatings to extended the lifetime of BPPs
- Results and lessons learned from this project will be used to improve corrosion-resistant coatings for BPPs available to the PEMFC industry