FORGE NANO

Highly Robust Low-PGM MEAs Based upon Composite Supports

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Forge Nano

University of Connecticut

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Project ID# FC168

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Overview

Timeline

- Project Start Date: 2/21/2017
- Project End Date: 11/20/2017

Budget

- FY17/Total Budget: $155,000

Barriers

- High voltage & high cycle carbon durability without significant performance impacts
- Economical scalability of thin film solution

Partners

- **Ugur Pasaogullari Research Group** Center for Clean Energy Engineering, University of Connecticut

Relevance

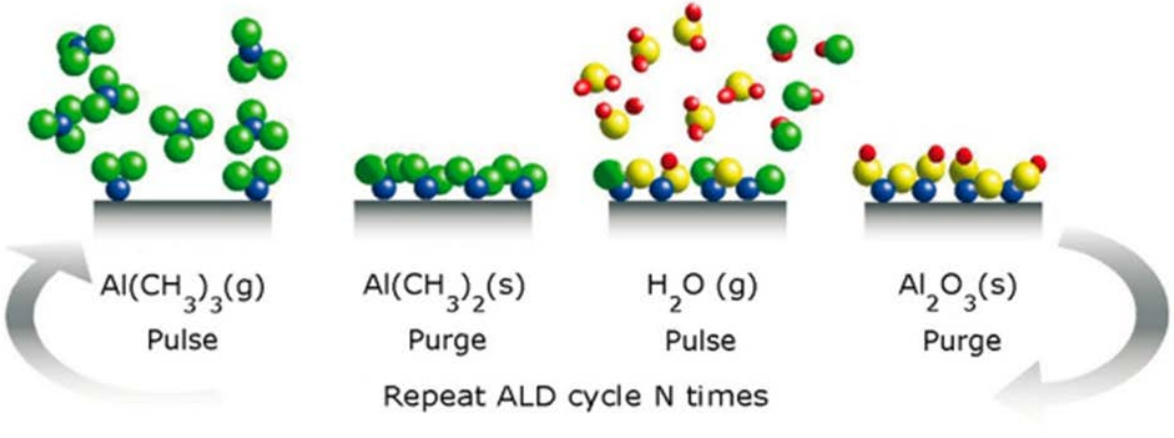
Specific Technical Objectives:

- Demonstrate a successful overcoat method on commercial low PGM Pt/C catalysts, specifically targeting uniform coverage of the carbon support with gas phase access to the Pt catalysts.
- Evaluate the activity, ohmic resistance and cycling stability of overcoated catalyst materials by rotating disk electrode (RDE) and membrane electrode assembly (MEA) testing.
- Demonstrate improved cycling durability with MEA testing of optimized encapsulated catalysts without significant loss in activity.
- Down select to a viable encapsulated Pt/C catalyst material based on performance, process scalability and techno-economic considerations.

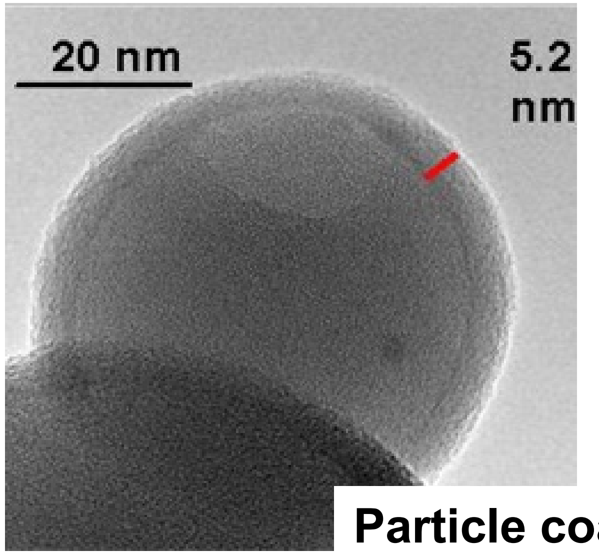
Impact:

- Achieve the 2020 targets for cost ($40/kW at the system level, $14/kW at the MEA level), start-up/shutdown durability (5,000 cycles), and less than 10% loss in power after 5,000 hours.

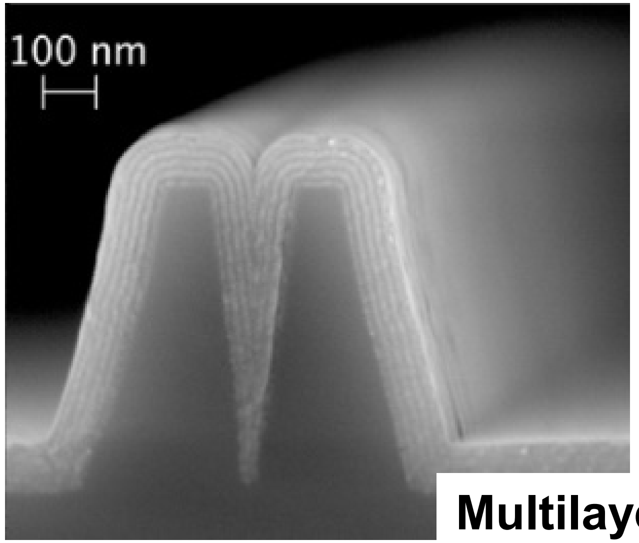
Approach:
Atomic Layer Deposition



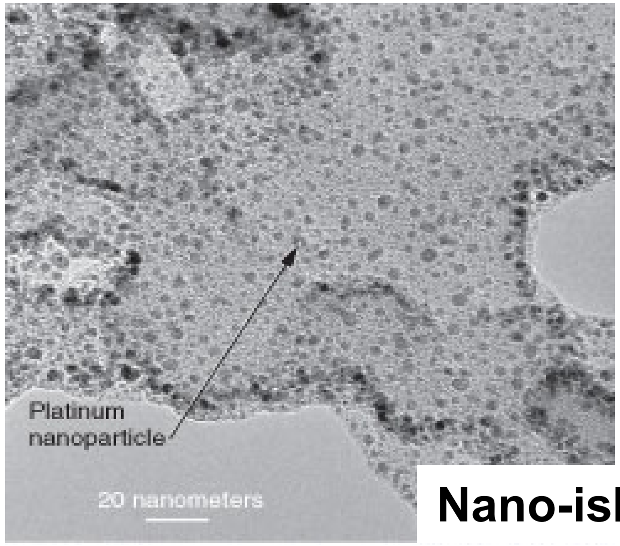
- Gas phase process
- Self limiting
- No line-of-sight restrictions
- Sub-nanometer control
- Pinhole free



Particle coatings

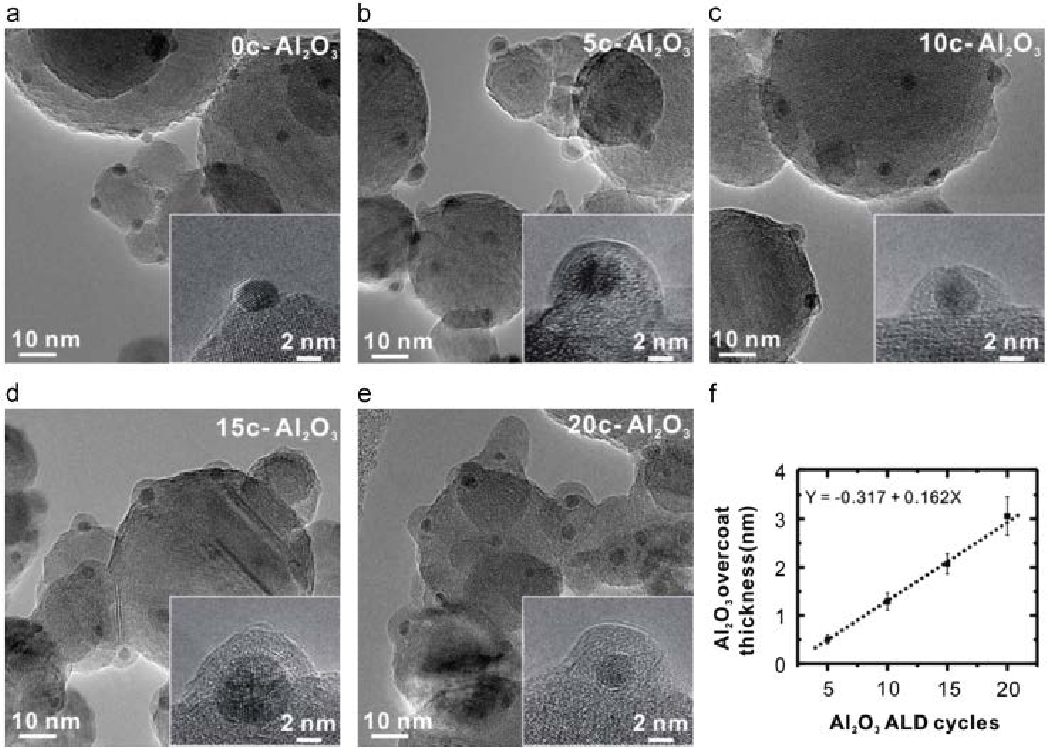


Multilayers

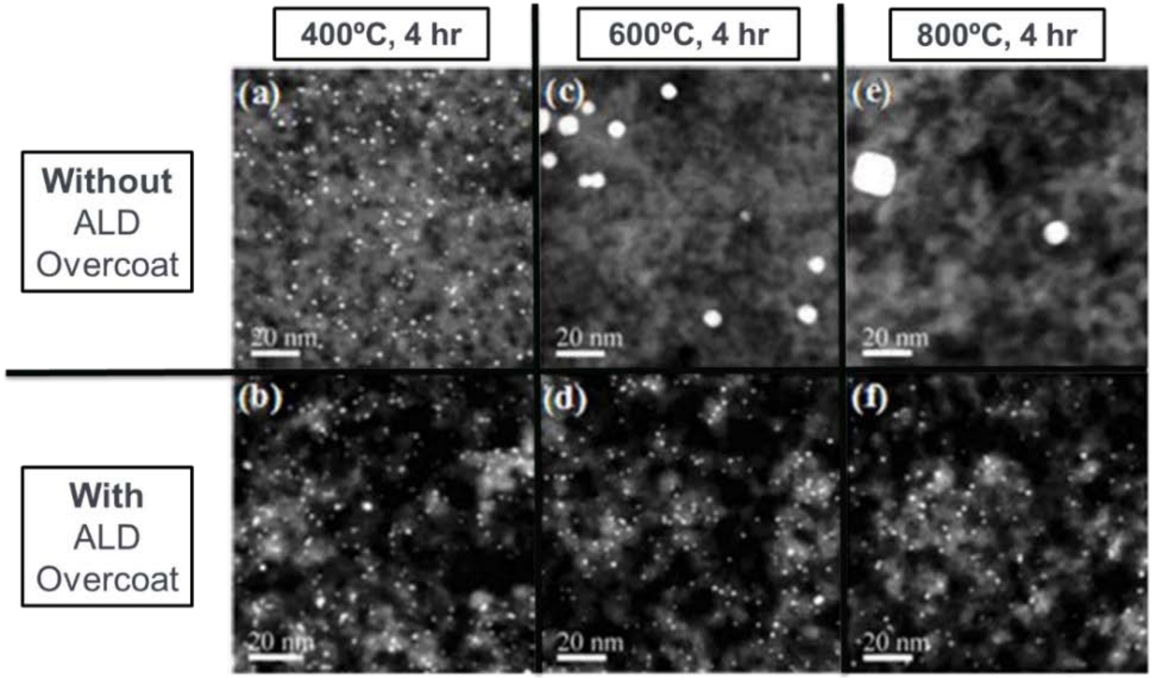


Nano-islands

Approach:
ALD for Better Durability



Pd:Al_2O_3 catalysts with 0-20 Al_2O_3 ALD overcoating cycles. [Lu et al., Surf Sci Reports 71 (2016) 410-472]

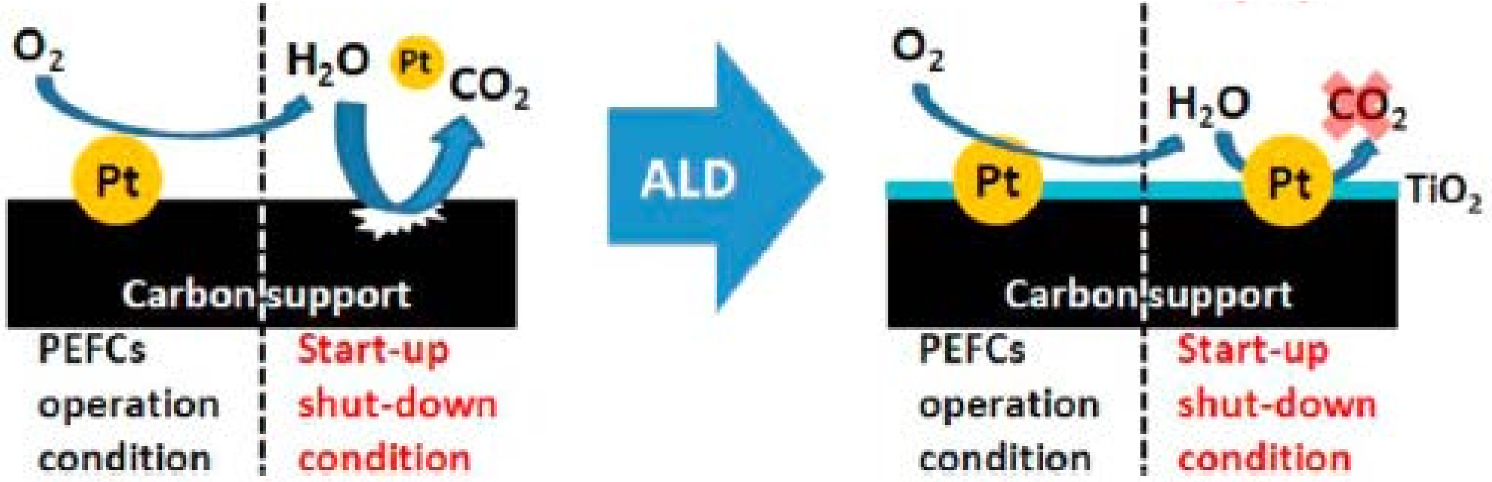


Al_2O_3 ALD overcoating on ALD-derived Pt nanoparticles, showing effective elimination of sintering/ripening at high temperatures. [Liang et al. ACS Catalysis, 1, (2011) 1162-1165]

We use ALD techniques to apply thin conductive coatings to the carbon surfaces to passivate them against electrochemical corrosion and to stabilize the electrochemically active structures.

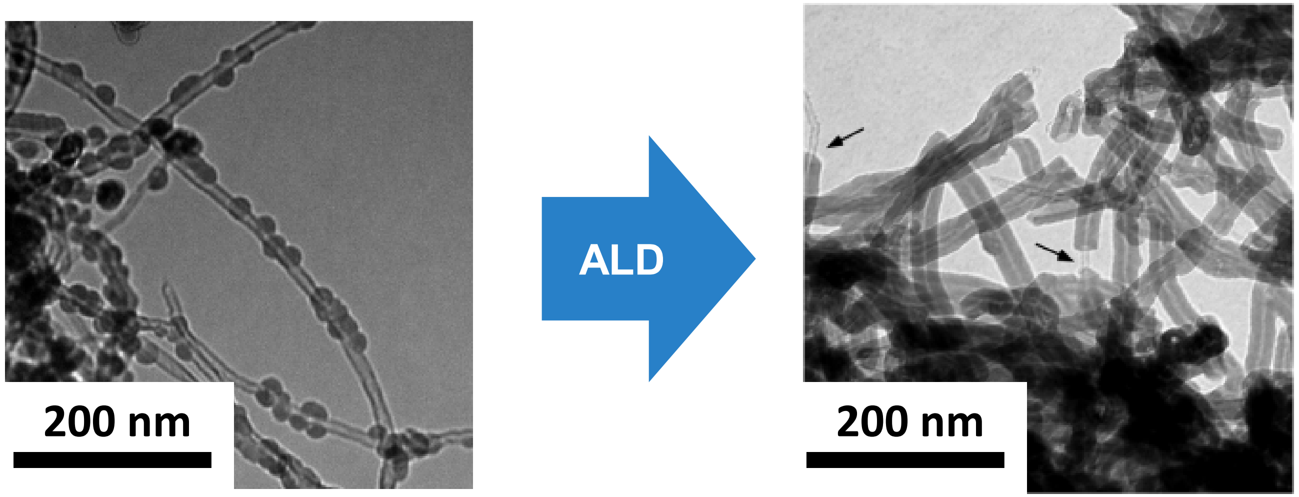
Approach:
Challenges

Engineering Selectivity:



[adapted from Chung et al., J. Energy Chem. 25 (2016) 258-264].

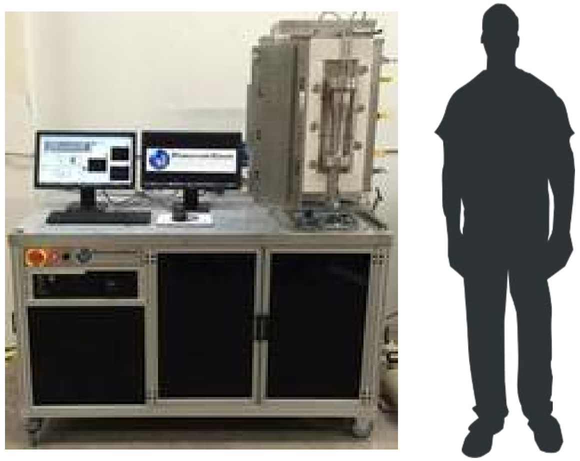
Overcoming Intrinsic Surface Effects:



[Sun et al. Journal of Physical Chemistry C, 117, 22497, 2013]

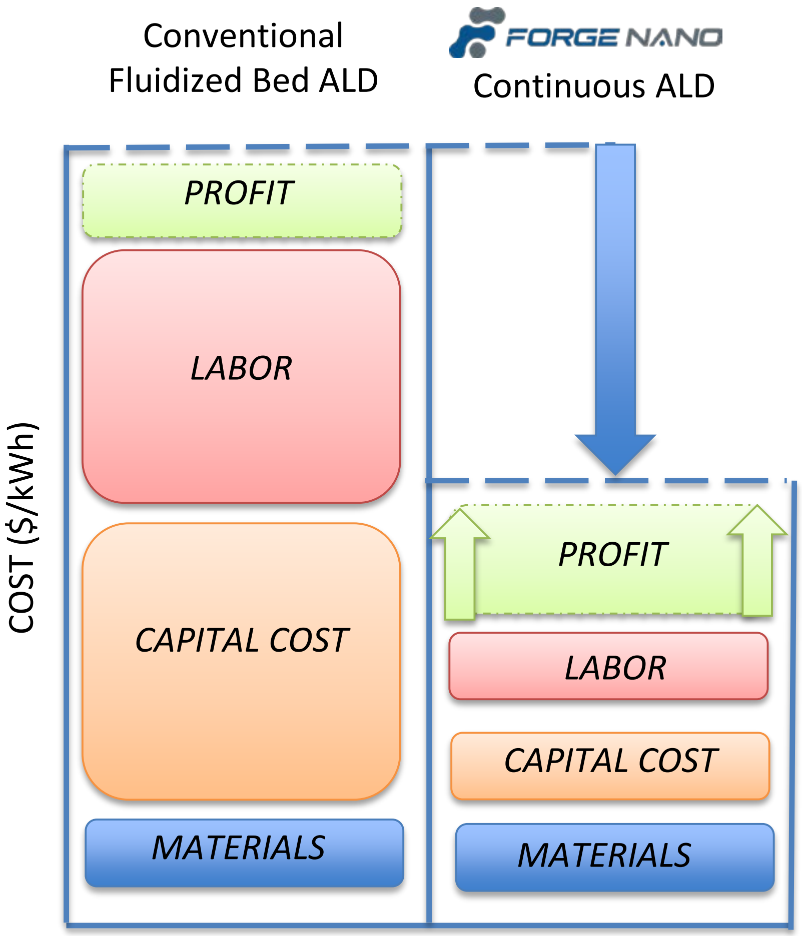
Approach:
Scaling

Forge Nano's lean manufacturing strategy significantly reduces labor and capital costs & minimizes waste



Conventional Batch System

High Throughput Continuous System



Approach:
Optimization Goals

- Process Parameters for quality coatings
  - Precursors (Halides, Metal alkyl, Aqueous oxidizers, Oxygen allotropes)
  - Diffusion Times
  - Purge Times
  - Pressure
- Thickness (ALD Cycles)
- Conductivity (ALD Doping and Concentrations)
- Nucleation (Carbon pretreatment & Pt blocking)
- Porosity of Coating (Annealing & Crystallinity)
- Atomic Contaminants (Halides)

Approach:
Optimization Measurements

- Catalyst electrochemical surface area (ECSA)
- Catalyst activity (mass and specific)
- Coating resistivity (electrochemical capacitance)
- Coating stability (over whole potential range of 0.6 to 1.0 V)
- Polarization curves
- Potential cycling (start/stop $1.0 < E < 1.5$ V versus RHE)
- Potential holds (1.2V vs RHE)
- Scaled measurements (MEA testing) (DOE 2011 Support Testing protocols)

Progress:
Sample Set 1

Sample Set 1 Target: Process conditions; appropriate scale for thickness; annealing impacts

ID	Date	ALD cycles	mass (g)	Precursor Temp	Precursor ΔP	Precursor Time	Precursor Purge	Ox ΔP	Ox Time	Ox Purge	Static or Flow	Process Notes	[M] (ppm)
FN0009.1-1	3/28/2017	3	2.5	40	9.7	2	10	7.1	2	10	flow		18603
FN0009.2-1	3/28/2017	3	2.5	40	8.8	2	10	8	2	10	flow	Ox predose	14732
FN0009.3-1	3/30/2017	50	5	40	9.5	2	10	7.9	2	10	flow		20648
FN0009.4-1	3/30/2017	50	split from 3.1	-	-	-	-	-	-	-	-	300C anneal 9.3	19078
FN0009.11-	3/31/2017	3	2.5	75	60	30s/10min	5-20-5	100	2min/ 10min	5-20-5	static		19938
FN0009.5-1	4/5/2017	50	5	50	20	35s/2min	2-8-2	35	30s	2-8-2	static		24388
FN0009.6-1	4/5/2017	50	split from 3.1	-	-	-	-	-	-	-	-	300C anneal 9.5	13865
FN0009.7	4/6/2017	27	5	50	13	35s/2min	2-8-2	40	30s	2-8-2	static		8416
FN0009.8	4/10/2017	27	split from 9.7	-	-	-	-	-	-	-	-	300C anneal 9.7	9591
FN0009.9	4/10/2017	9	2.5	50	20	15s/1min	1-4-1	35	15s	1-4-1	static		12331
FN0009.10	4/11/2017	9	2.5	75	56	30s/10min	8-30-5	100	2min/ 10min	5-20-5	static		12182

Progress:
Sample Set 1

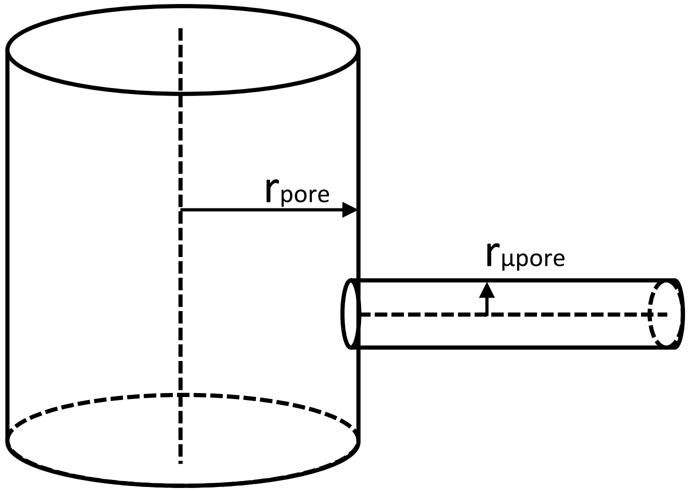
Sample Set 1 Target: Process conditions; appropriate scale for thickness; annealing impacts

$A = 2\pi rh + \cancel{2\pi r^2}$

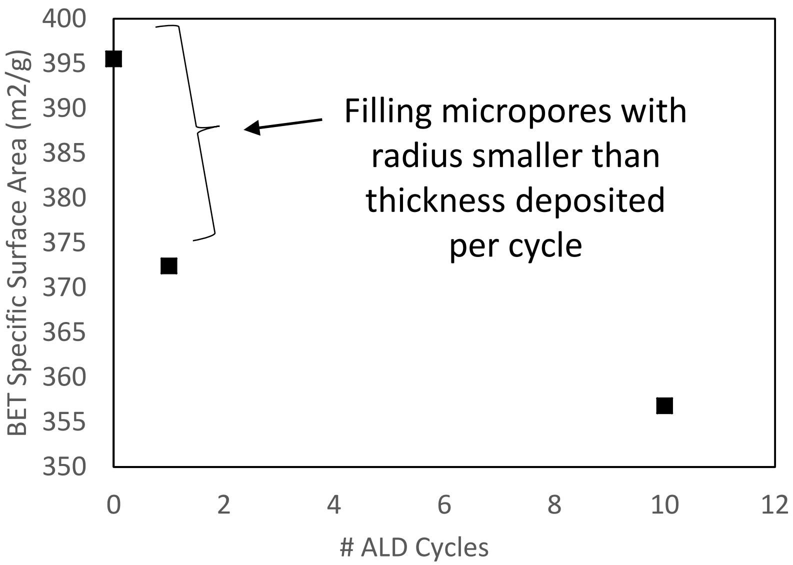
0

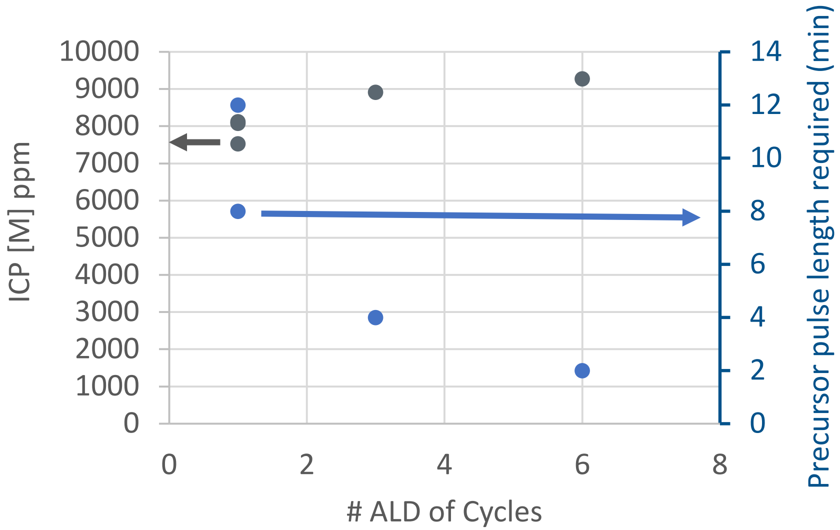
A = Area
r = radius
h = height
h >> r

$A = 2\pi r_{pore}h_{pore} + 2\pi r_{\mu pore}h_{\mu pore}$



Process optimization experiments using high surface area carbon as a strawman





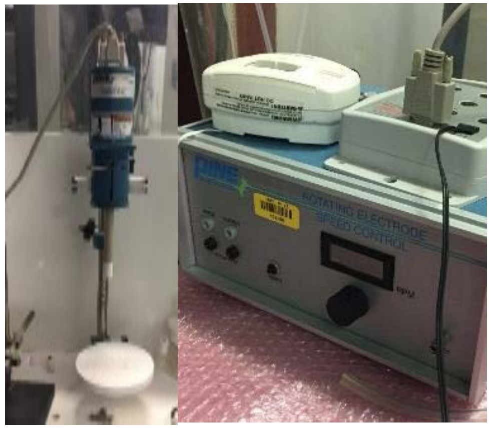
First ALD cycles fill micropores and deposit at higher growth rates. Subsequent cycles display consistent growth rates.

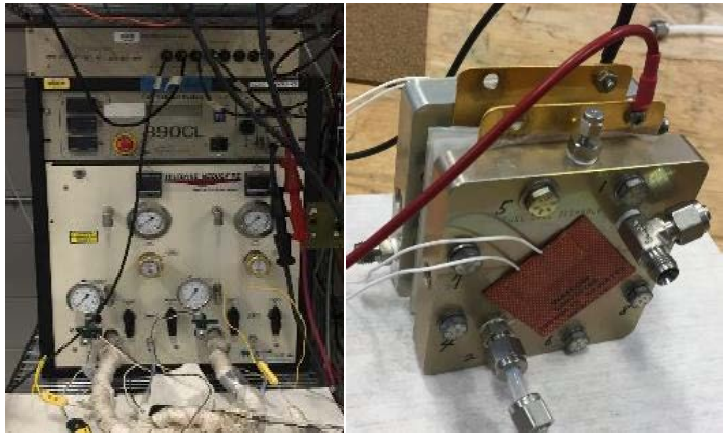
Progress
Future Targets

- **Sample Set 1 Target:** Appropriate scale for thickness; annealing impacts
- **Sample Set 2 Target:** Explore alternative precursors and doping/conductivity
- **Sample Set 3 Target:** Optimize thickness and process conditions based on RDE measurements for Set 1 and Set 2
- **Sample Set 4 Target:** Optimized film conductivity and porosity with postprocessing annealing
- **Sample Set 5 Target:** Reproducibility

Collaboration: Measurements Support

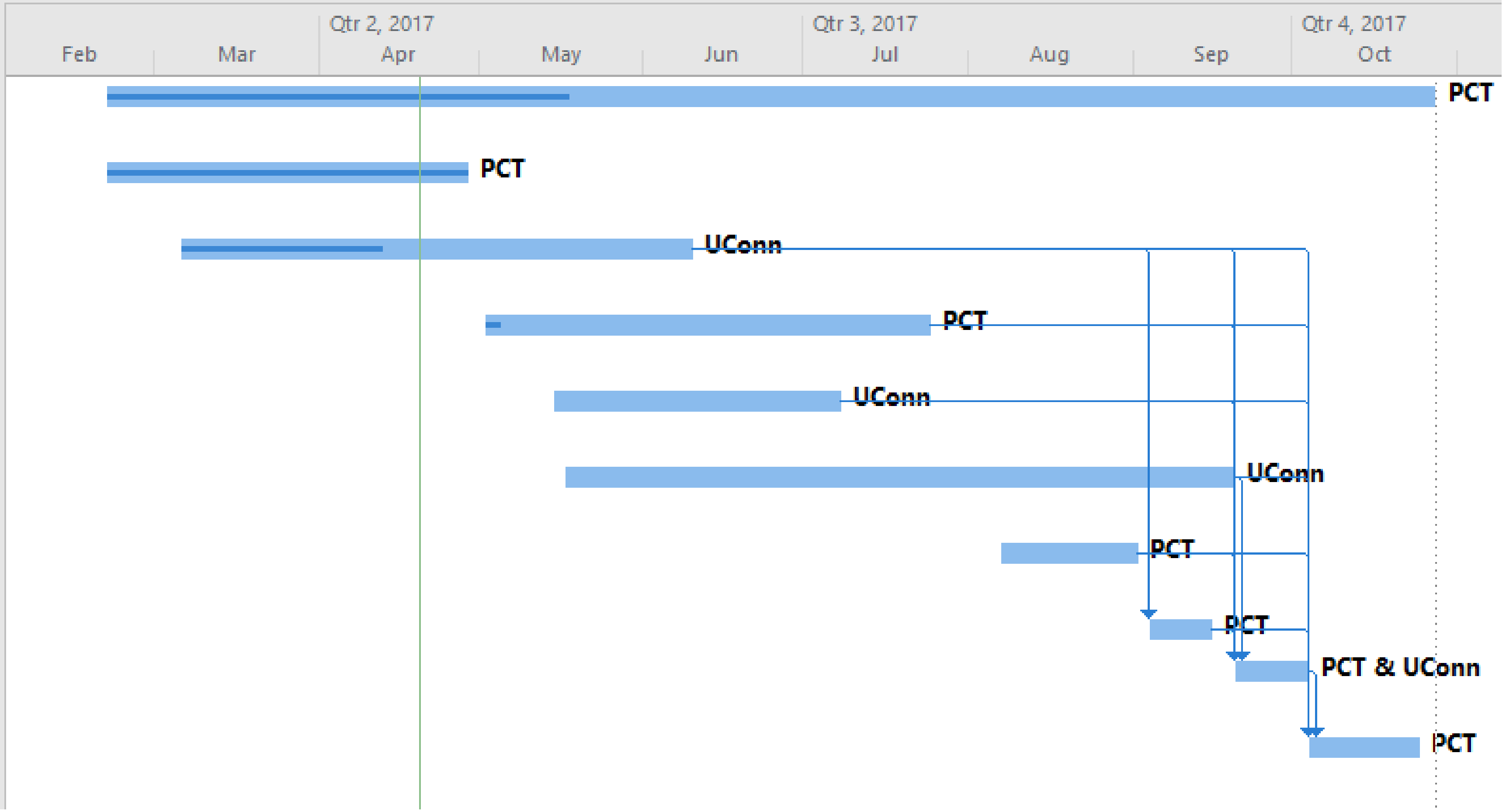
- Ugur Pasaogullari Research Group
  - Center for Clean Energy Engineering @ University of Connecticut
  - Subcontract
  - Electrochemical Characterization
- Pasaogullari Group is primarily providing RDE characterization of the coated electrode materials to understand and validate the effects of the coatings/processes.
- Secondarily, they will do MEA testing of selected/optimized materials to establish baseline and to help with final down selection of coatings/processes for Phase II.





Schedule:
On Track

Task Name	Duration
Task 1: Project Management and Customer Development	9 mons
Task 2: ALD Pt/C commercial catalysts	2.5 mons
Task 3: RDE Evaluation of initial ALD on Pt/C	3.5 mons
Task 4: Optimization of ALD on Pt/C powders	3 mons
Task 5: Evaluation of Optimized Materials	2 mons
Task 6: Evaluation of Materials by MEA Durability Cycling	4.5 mons
Task 7: (If required): ALD layers for enhanced conductivity	1 mon
Task 8: Economic Assessment	2 wks
Task 9: Final down-selection for Phase II readiness	2 wks
Phase I Report and Phase II Proposal	3 wks



Proposed
Phase I/II Targets

- Technoeconomic feasibility study for optimized ALD process and post processing conditions
- Scaled demonstration and development of scaled equipment for temperatures and pressures required. Include post processing.
- Expanded lifetime testing on scaled optimized catalysts

Summary

- Developing strategies to stabilize the electroactive catalyst and the carbon support with ALD thin films
- Coating optimization includes ALD film growth process, film conductivity, film porosity and post process annealing
- Measurements target carbon corrosion during start stop conditions as well as performance metrics (ESCA, activities) at RDE and MEA scale
- This work is a collaboration between Forge Nano and Pasaogullari Research Group at University of Connecticut