Catalyst Layer Design, Manufacturing and In-line Quality Control

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Project ID # TA027

Overview

Timeline

- ❑ Project Start Date: 10/1/18
- ❑ Project End Date: 10/1/20

Budget

- ➢ DOE funding released: 12/14/18
- ➢ Total project budget: $2.5M
  - ➢ DOE funding: $2M
  - ➢ UConn cost share: $500K
- ➢ Total DOE funds spent*: $1,084,318

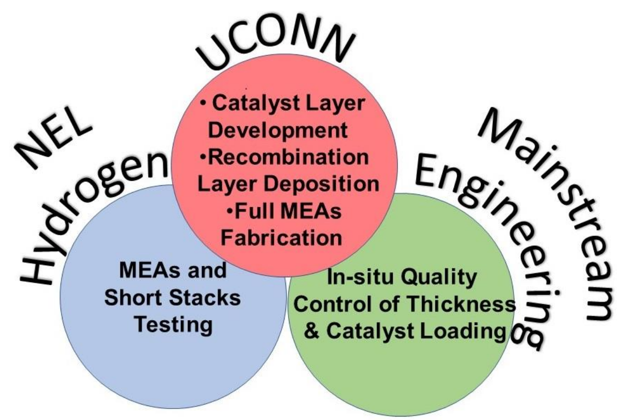
* As of 12/31/2019

Barriers

Hydrogen Generation by Water Electrolysis

Barrier	Target
F. Capital Cost	< $2.00 $/kgH_2$
G. System Efficiency and Electricity Cost	75 %
K. Manufacturing	680 cm^2 (MEA)

Partners



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Relevance

Overall objective:

Demonstrate the capabilities of the Reactive Spray Deposition Technology (RSDT) for direct catalysts deposition and fabrication of large scale (680 cm^2) membrane electrode assemblies (MEAs) that meet the performance, manufacturing, and cost reduction targets.

Specific objectives for the current period (Jan. – Dec. 2019):

- Develop a recombination layer to decrease hydrogen permeation <10 %LFL. **(100%)**
- Demonstrate performance on 86 cm^2 MEAs with ten times reduced catalyst loadings within 50 mV of baseline commercial electrodes at 1.8 A/cm^2. **(100% accomplished)**
- Demonstrate stability of the MEAs for over 1000 hours. **(100% accomplished)**
- Optimize RSDT parameters for fabrication of full 86 cm^2 MEA.**(100% accomplished)**

Barriers	Impacts
F. Capital cost	Cost reduction with RSDT process: **10X catalyst loading reduction.**
G. System efficiency and electricity cost	Development of high-performance electrolyzer MEA. Reduce electric power consumption 50 % and improve the cell efficiency to 70 % (1.48 V/2.1 V, Nafion 117 + Nafion 211).
K. Manufacturing	Scale-up manufacturing at 680 cm^2 cell stack level coupled with in-line quality control. Achieve stability of >1000 hours at 1.8 A/cm^2, 50 ^oC and 400 psi differential pressure.

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Approach - Project Overview

Budget Period I: CCM optimization and development of quality control methods (Year 1)

Budget Period II: Scale-up manufacturing, real-time quality control and laser diagnostics (Year 2)

Tas k#	Project Activity	Year 1				Year 2			
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
1.0	Optimization of RSDT process for **recombination layer** deposition								
2.0	Full RSDT **catalyst coated membrane** development and evaluation				86 cm^2				
3.0	**Multi-scale characterizations** of catalyst: (real time quality control and laser system)		86 cm^2				680 cm^2		
4.0	**Scale-up** of electrode manufacturing				86 cm^2		680cm^2		
5.0	**Commercial-scale** design			86 to 680 cm^2					
6.0	**In-line quality control** of CCM fabrication			86 cm^2			680 cm^2		

Deliverables

- ✓ **Scale-up CCMs to 680 cm^2 with 0.2 mg_{Pt}/cm^2 and 0.3 mg_{Ir}/cm^2 catalyst loading on the cathode and anode.**
- ✓ **Durability of >1000 hours at 1.8 A/cm^2, 50 ^oC and 400 psi.**

Approach – Budget Period I Milestones

#	Milestone Description/Go-No Go Decision	Date	%Complete
1.1	Verify the recombination layer effectively reduces the hydrogen crossover bellow 10% LFL.	Q2 July, 2019	100 % completed
2.1	Fabricate 86 cm^2 full MEAs with 10 times less catalyst loadings and show similar performance with commercial MEA.	Q5, March, 2020	100% completed
2.2	Demonstrate stability of >1000 h with optimized cathode, anode, and recombination layers. (Go-No Go decision)	Q5, March, 2020	100% completed
3.1	Demonstrate laser system installed, calibrated and operational for in-situ analysis.	Q4, Dec., 2019	100% completed
6.1	Demonstrate in line quality control system installed and operational on RSDT equipment.	Q3, Sept., 2019	100% completed
6.2	Catalyst loading measurement sensitivity of 0.03 mg_{Pt}/cm^2 verified with inductively ICP analysis and compared to in-situ measurements on 86 cm^2 MEAs.	Q5, March, 2020	100% completed

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Approach – Budget Period II Milestones

#	Milestone Description	Date	%Complete
3.2	Determine the optimal Ir concentration by using the Raman spectra of IrO_x particles in the RSDT flame.	Q5 April, 2020	20 % completed
3.3	Determine the optimal Pt concentration by using the Raman spectra of particles in the RSDT flame.	Q5 April, 2020	20 % completed
4.1	Optimize the cathode, anode, and recombination layer and scaled up the MEAs to 680 cm^2 active area.	Q6, May, 2020	30% completed
4.2	Demonstrate comparable performance of the full scale 680 cm^2 RSDT MEA with the 86 cm^2 MEA.	Q6, June, 2020	0% completed
4.3	Demonstrate durability of >1000 h with optimized cathode, anode, and recombination layers for full scale 680 cm^2 MEAs.	Q8, Dec., 2020	0% completed
6.3	Confirm catalyst loading measurement sensitivity of the quality control system on 680 cm^2 MEAs.	Q6, June, 2020	0% completed
6.4	Collect in-situ high resolution images on 680 cm^2 MEAs and verify repeatability of less than 10% standard deviation.	Q6, July, 2020	0% completed

End of project goal:

Manufacturing of scale-up CCMs of 680 cm^2 with 10% the catalyst loading of commercial MEAs and achieving electrolyzer stability of >1000 hours

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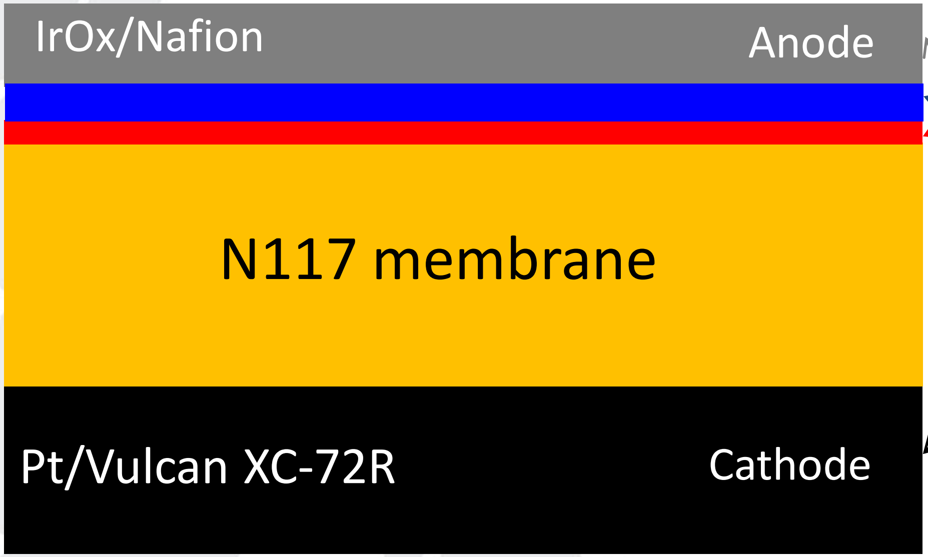
Recombination Layer (RL) Deposition

Schematic of RSDT fabricated CCM



CCM fabrication steps:

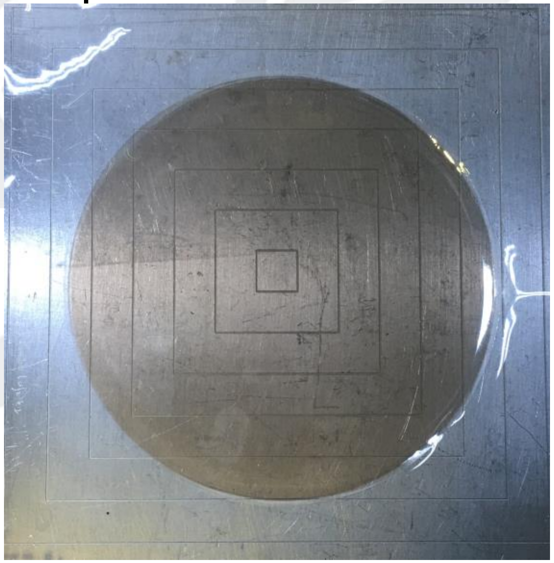
Step 1: RSDT Pt RL deposition on top of N117 membrane.

Step 2: Lamination (hot pressing) of Nafion 211 membrane on top of the Pt RL.

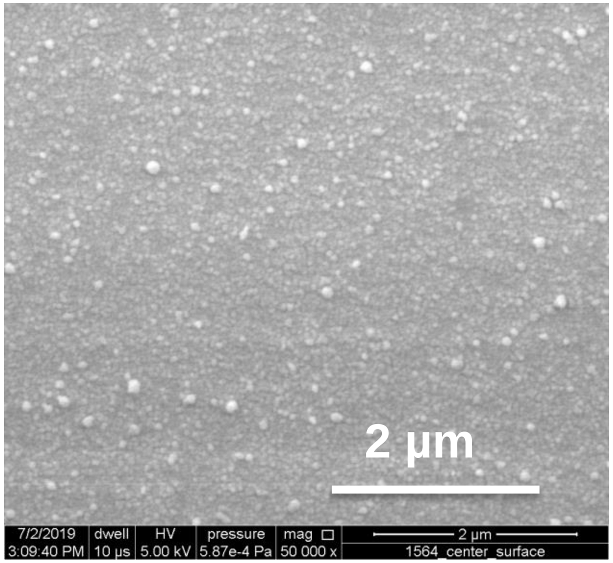
Step 3: RSDT cathode catalyst (Pt/C) deposition (0.2-0.3 mg_{Pt}/cm^2, thickness: 15-20 µm Pt particle size: ~2nm).

Step 4: RSDT anode catalyst (IrO_x) deposition (0.2-0.3 mg_{Ir}/cm^2, 2-2.5 µm, IrO_x particle size: 1 - 2 nm).

Picture of 86 cm^2 RL deposited on Nafion 117



Topography of the RL



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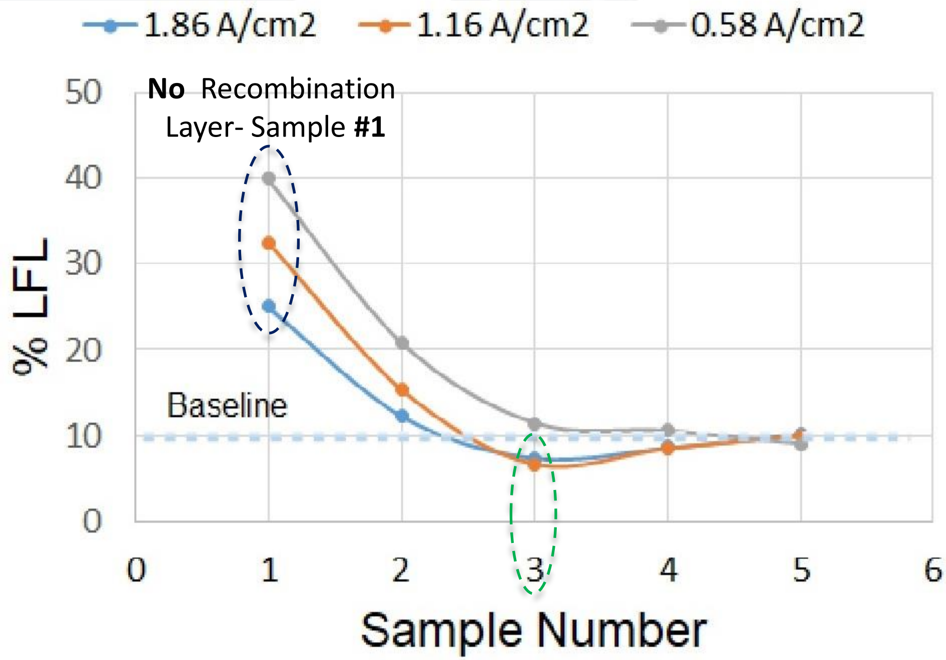
Performance of RSDT-fabricated recombination layer

Cathode: commercial GDE, Pt loading 3 mg cm^{-2}, anode commercial GDE, Ir loading, 3 mg cm^{-2}; Membrane: N117, 50 ºC, 400 psi differential pressure; Active area: 86 cm^{2}.

The effect of Pt loading in the recombination layer on H_2 crossover



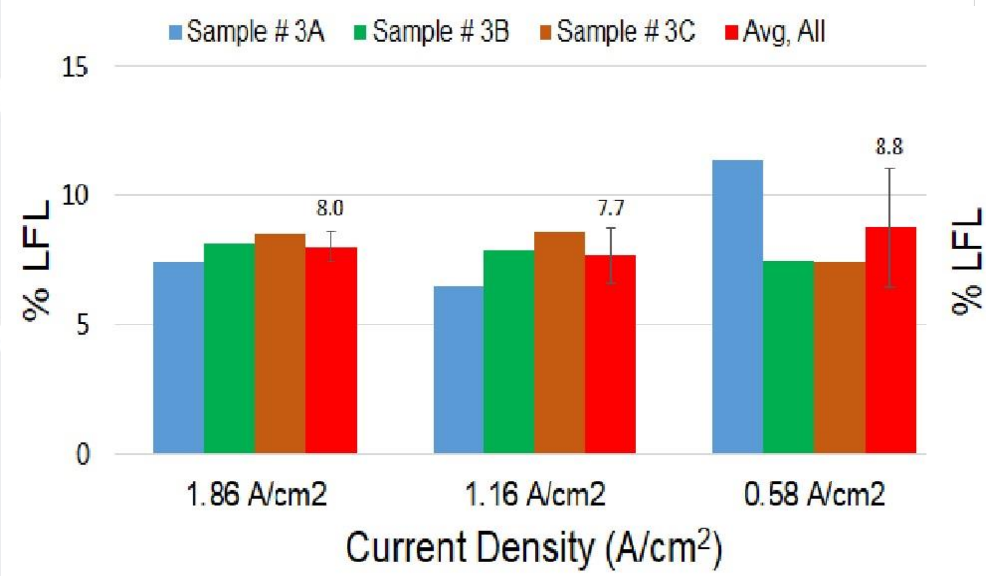
Sample	Recombination layer	Pt loading, Relative scale	Fabrication method	Nafion top layer thickness, µm	Nafion top layer fabrication method
1	No	NA	NA	NA	NA
2	Yes	Type 1, 1x loading	RSDT	6	RSDT spraying
3	**Yes**	**Type 1, 1x loading**	**RSDT**	**25**	**Nafion® N111 membrane**
4	Yes	Type 2, 2x loading	RSDT	25	Nafion® N111 membrane
5	Yes	Proton commercial	Proton commercial	Proton commercial	Proton commercial

- RSDT recombination layers are effective at both 1X (Sample 3) and 2X (Sample 4) Pt loadings and comparable to commercial product (Sample 5).
- The Pt loading for full RSDT-fabricated MEAs will be at 1X loading.

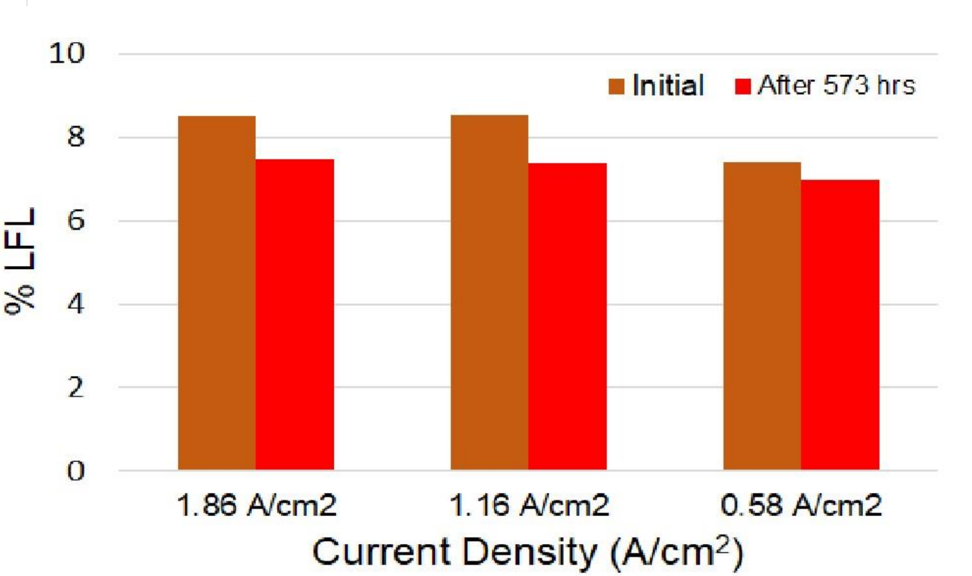
Performance of RSDT-fabricated recombination layer

Cathode: commercial GDE, Pt loading 3 mg cm^{-2}, anode: commercial GDE, Ir loading, 3 mg cm^{-2}; Recombination layer: 1X Pt loading, Membrane: N117, 50 ^{o}C, 400 psi differential pressure; Active area: 86 cm^2.

Reproducibility of H_2 crossover reduction as compared between 3 independent fabrications



Stability of H_2 crossover reduction



- The H_2 crossover reduction is reproducible among three independent fabrications.
- The H_2 crossover reduction has improved after 573 hours of operation at 1.8 A/cm^2, 50^{o}C, and 400 psi differential pressure, as a result of the activation of the Pt RL.
- All measured H_2 concentrations reached the lower limit of the test apparatus (10% LFL)

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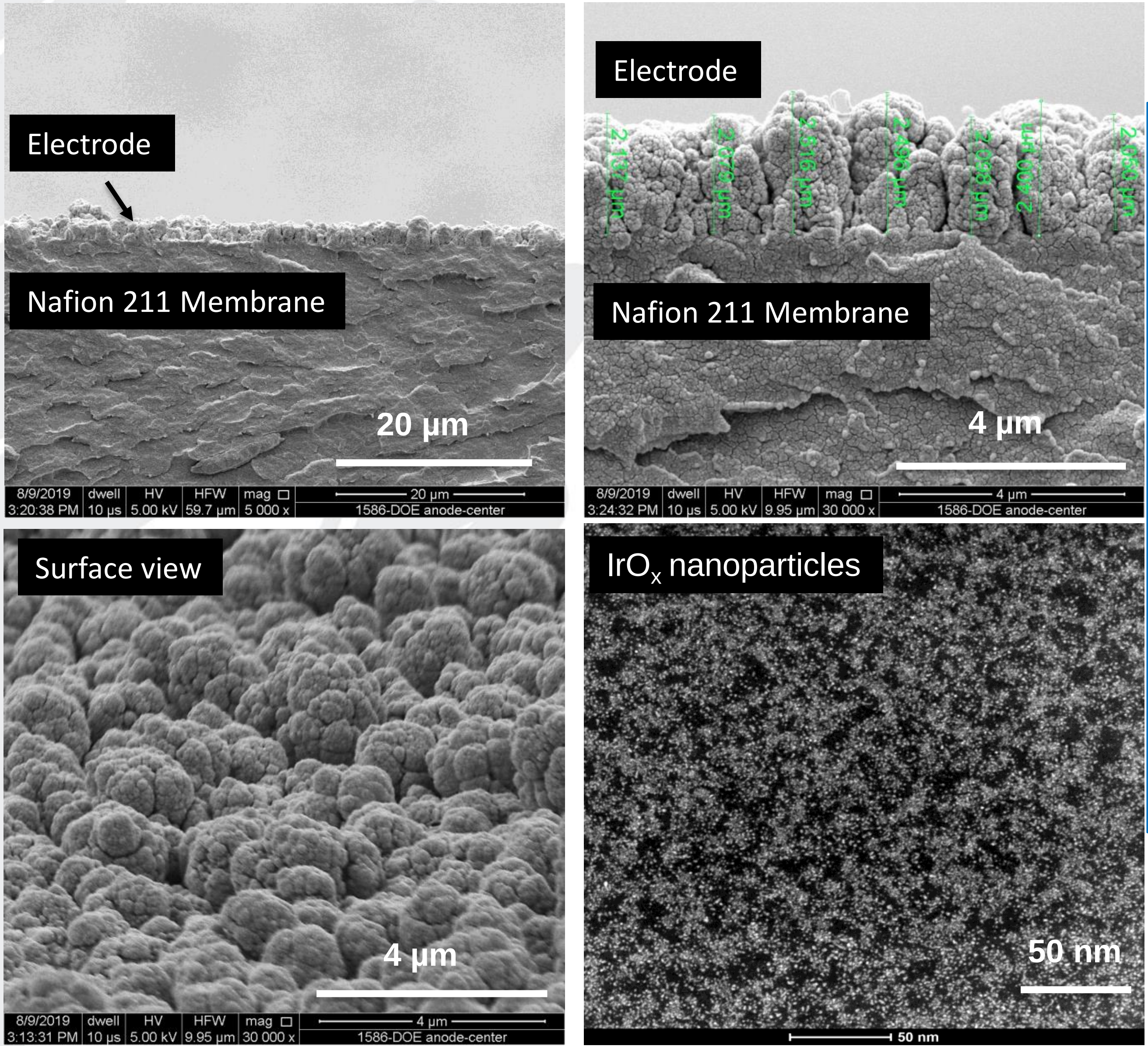
Characterization of RSDT-fabricated IrO_x anode catalyst layer



- Ir loading: 0.2-0.3 mg/cm^2
- Anode thickness: 2-2.5 µm
- Avg. IrO_x particle size: 1-2 nm
- The surface morphology of IrO_x anode layer is uniform, consisting of small agglomerated particles
- The anode layer is well adhered to the N211 substrate

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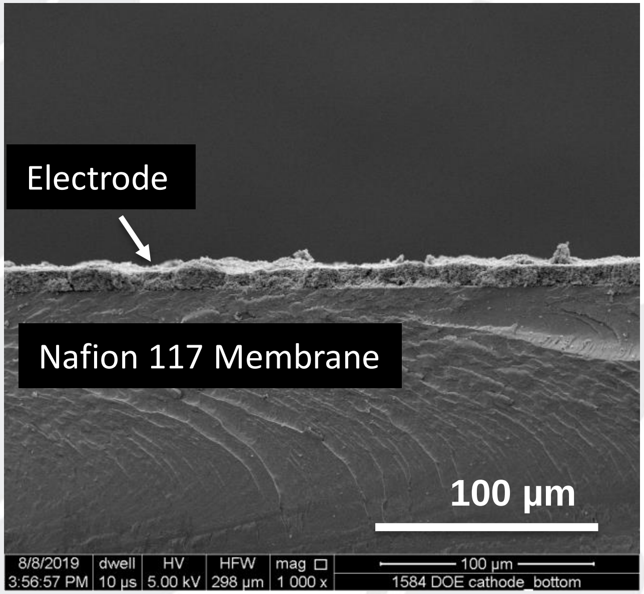
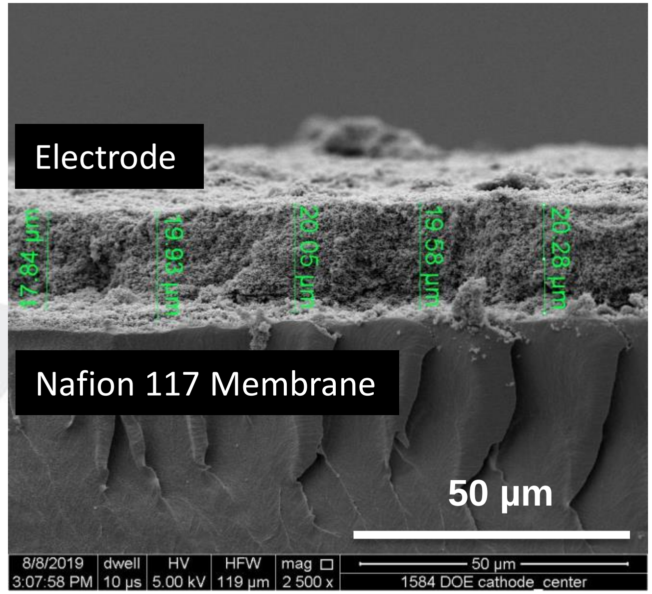
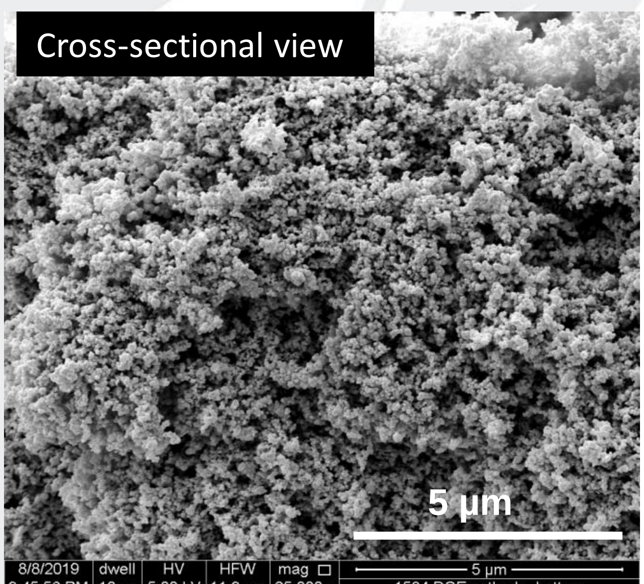
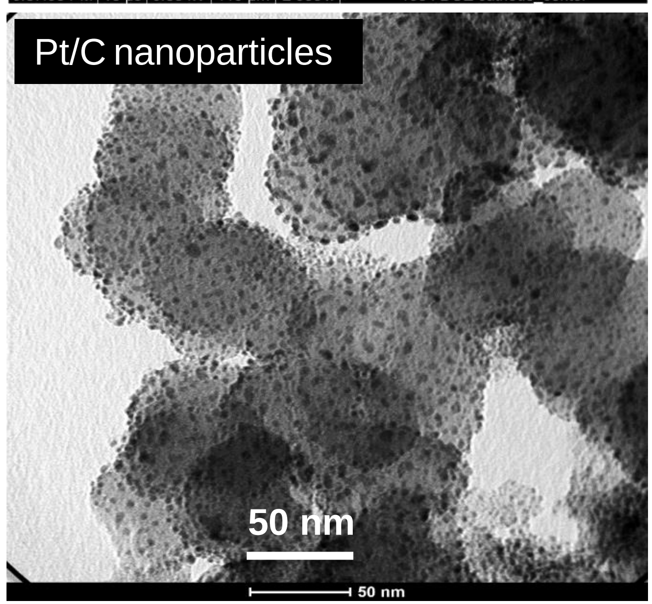
Characterization of RSDT-fabricated Pt/C cathode catalyst layer









- Pt loading: 0.2-0.3 mg/cm^2
- Cathode thickness: 15-20 µm
- Avg. Pt particle size: ~2 nm
- The Pt/C cathode layer has a porous structure
- The cathode layer is well adhered to the N117 substrate
- Pt nanoparticles are well dispersed on the carbon support particles

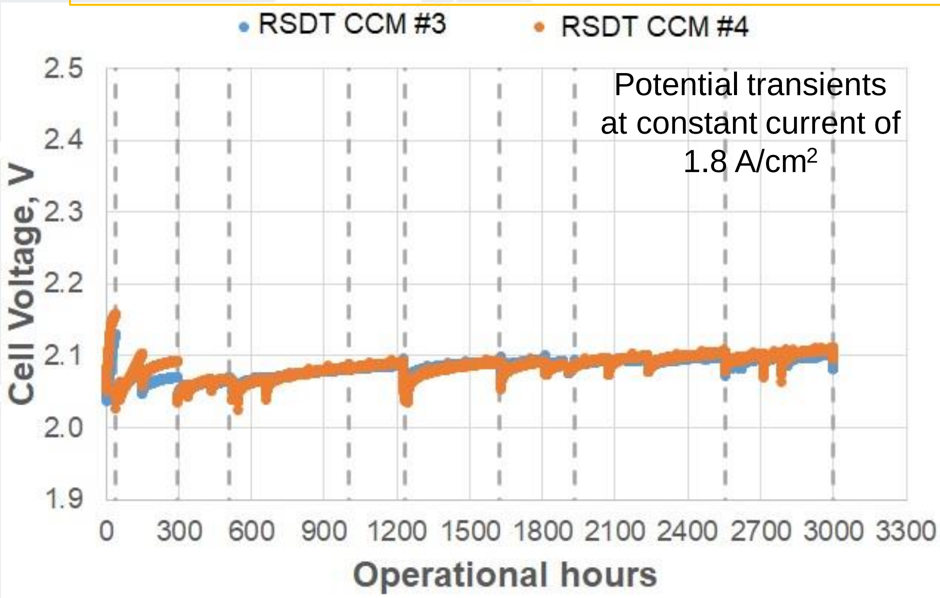
Accomplishments and Progress

Performance of RSDT-fabricated MEAs

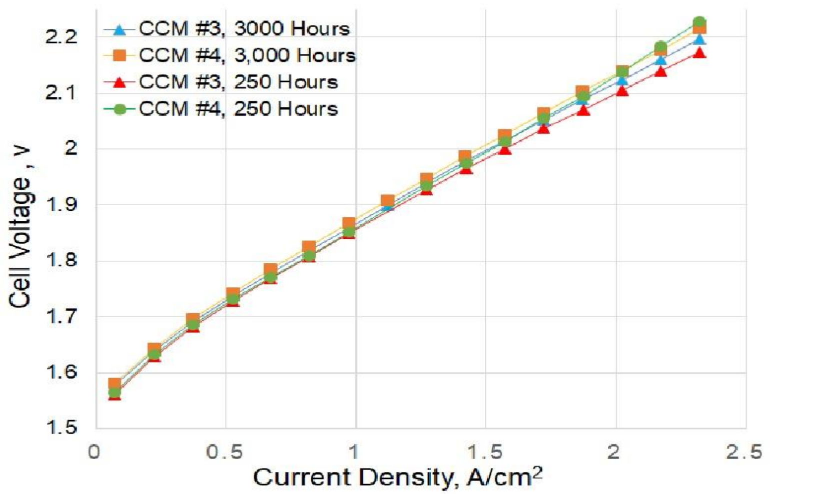
Milestone for stability of 86 cm^2 MEA exceeded by 3 times!

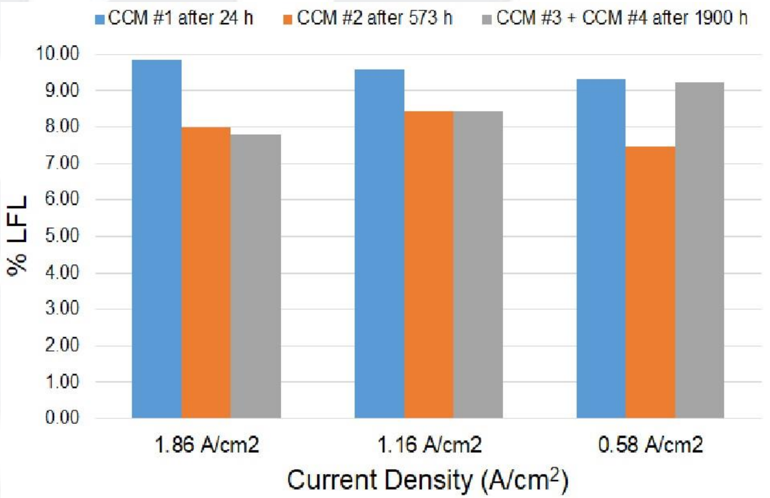
Stability test of a 2-cell stack: half RSDT anode (#3) and full RSDT MEA (#4)

Commercial GDE (#3): Pt 3 $mg_{Pt}\,cm^{-2}$ RSDT cathode (#4): Pt/Vulcan XC-72R, 0.2 $mg_{Pt}\,cm^{-2}$, I/C ratio 0.15;RSDT anode, Ir loading, 0.3 mg cm^{-2}; RSDT recombination layer: 1X Pt loading, membrane: N117, 50 °C, 400 psi differential pressure; active area: 86 cm^2.



Polarization curves measured after 250 h and 3000 h.





H_2 crossover measured after 1900 h of operation.

- As of March 23rd, the 2-cell stack had been operated for over 3000 hours (target 1000 hours).
- The polarization performance shows no significant loss at 3000 hours compared to at 250 hours when the MEAs were stabilized.
- The Pt recombination layer in MEA #3 and #4 remain effective for H_2 crossover reduction.
- **The BP I Go/No-Go criteria has been met.**

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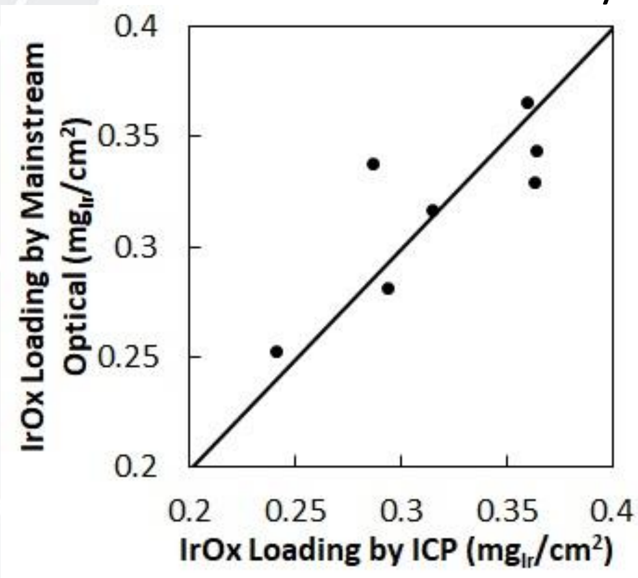
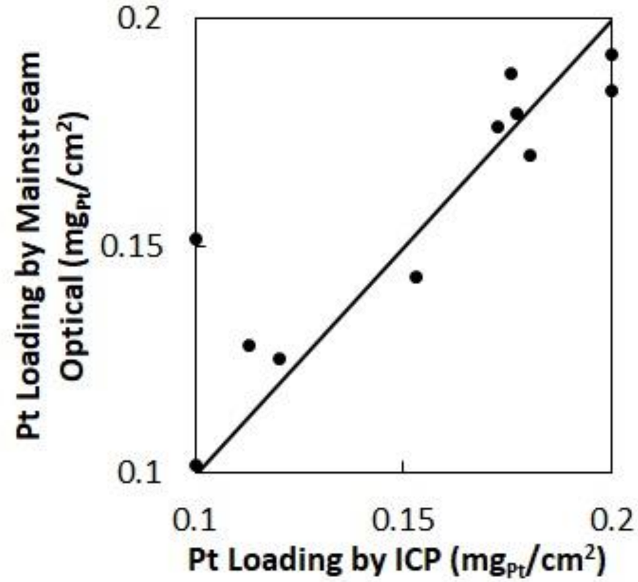
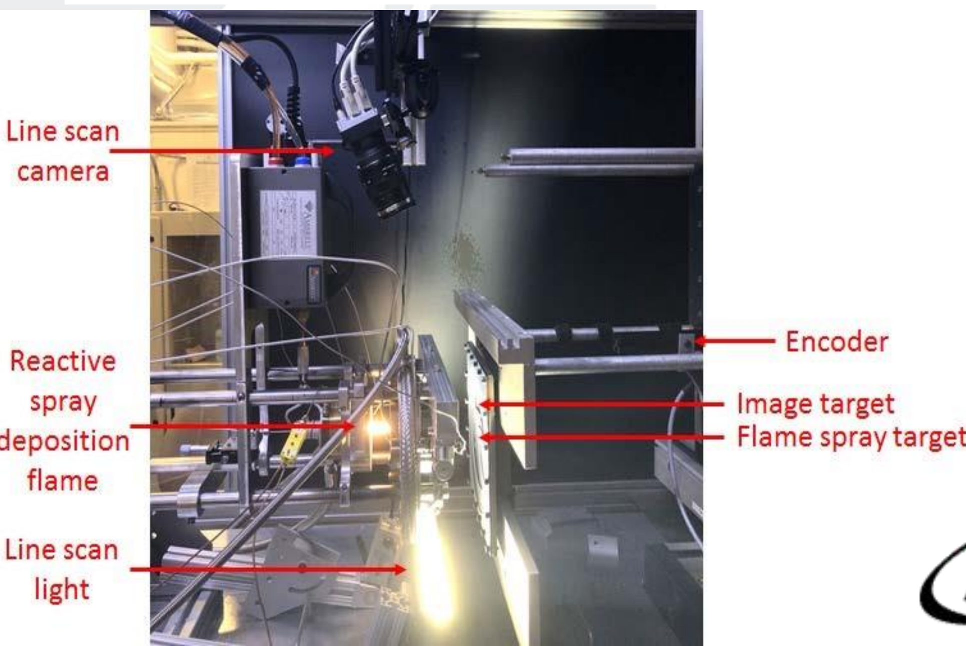
Installation of quality control equipment and in-situ catalyst loading measurement on RSDT II

Measurement of catalyst loading: optical vs. inductively coupled plasma (ICP)





- Catalyst loading measurement by optical reflectance at Mainstream and ICP analysis at UConn are compared.
- The root mean square error of calibration is 0.02 mg_{Pt}/cm^2 and 0.03 mg_{Ir}/cm^2 with respect to the diagonal line. (Milestone 6.2 is met.)



- Mainstream performed a test installation at UConn to image the RSDT process in real time.
- Evolution of a bulge/crack and spots on the electrode during fabrication was observed in the time-series of collected images.
- Issues encountered during operation are identified, such as vibration, focus of camera, and uneven lighting. Mainstream is working on modifying /designing hardware to resolving these issues.

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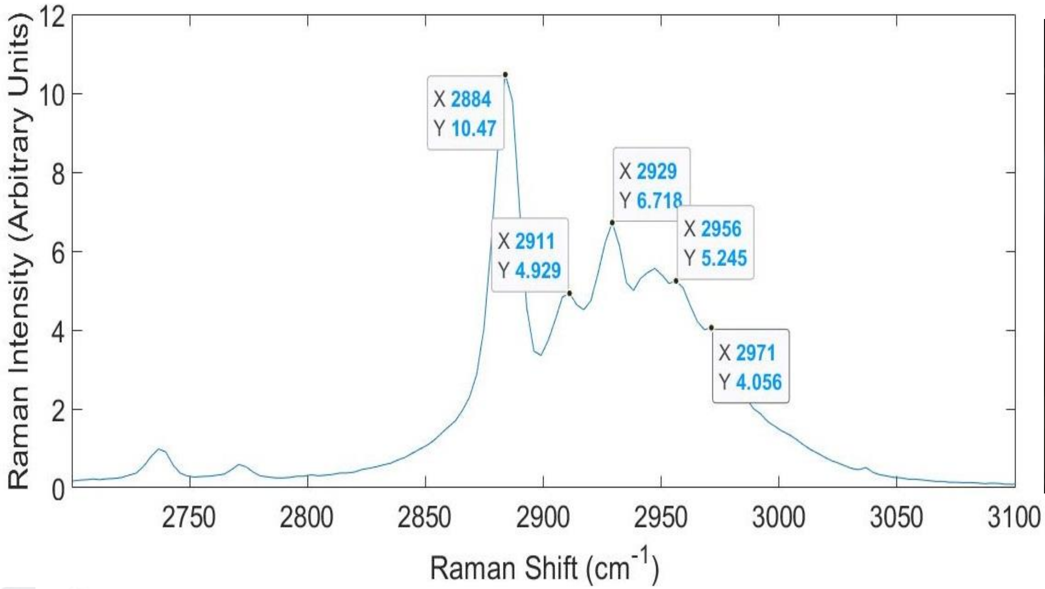
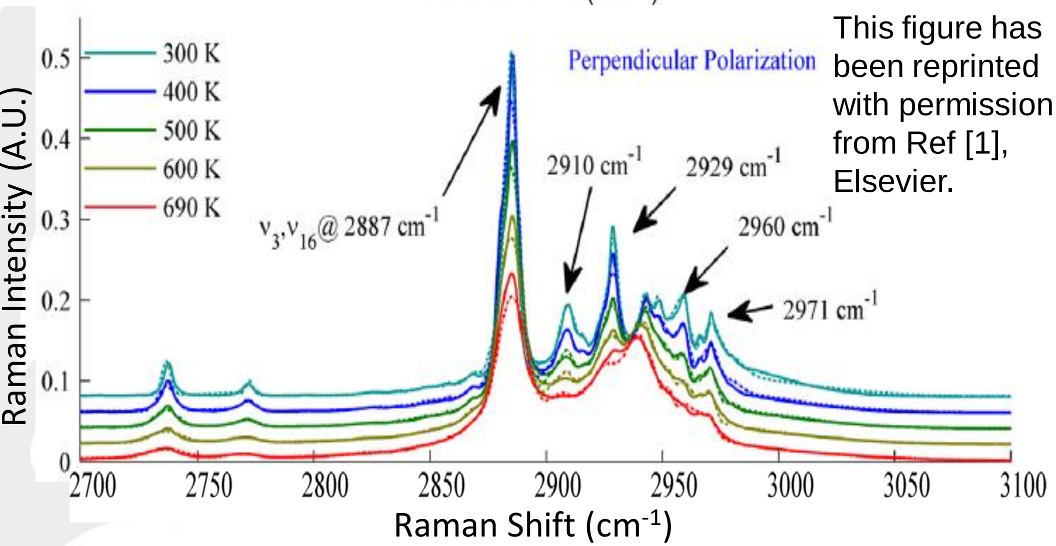
Set up and calibration of the laser equipment





This figure has been reprinted with permission from Ref [1], Elsevier.

- Standard propane gas calibration was performed using a laser wavelength of 532 nm at room temperature.
- Comparison of Raman spectra collected from propane using RSDT laser setup are consistent with those from literature [1].
- In-situ Raman analysis of the RSDT flame will be performed to characterize nanoparticle crystallinity and composition during anode (IrO_x) and cathode (Pt) depositions.

[1] Magnotti, G., KC, U., Varghese, P.L. and Barlow, R.S., 2015. Raman spectra of methane, ethylene, ethane, dimethyl ether, formaldehyde and propane for combustion applications. *Journal of Quantitative Spectroscopy and Radiative Transfer*, *163*, pp.80-101.

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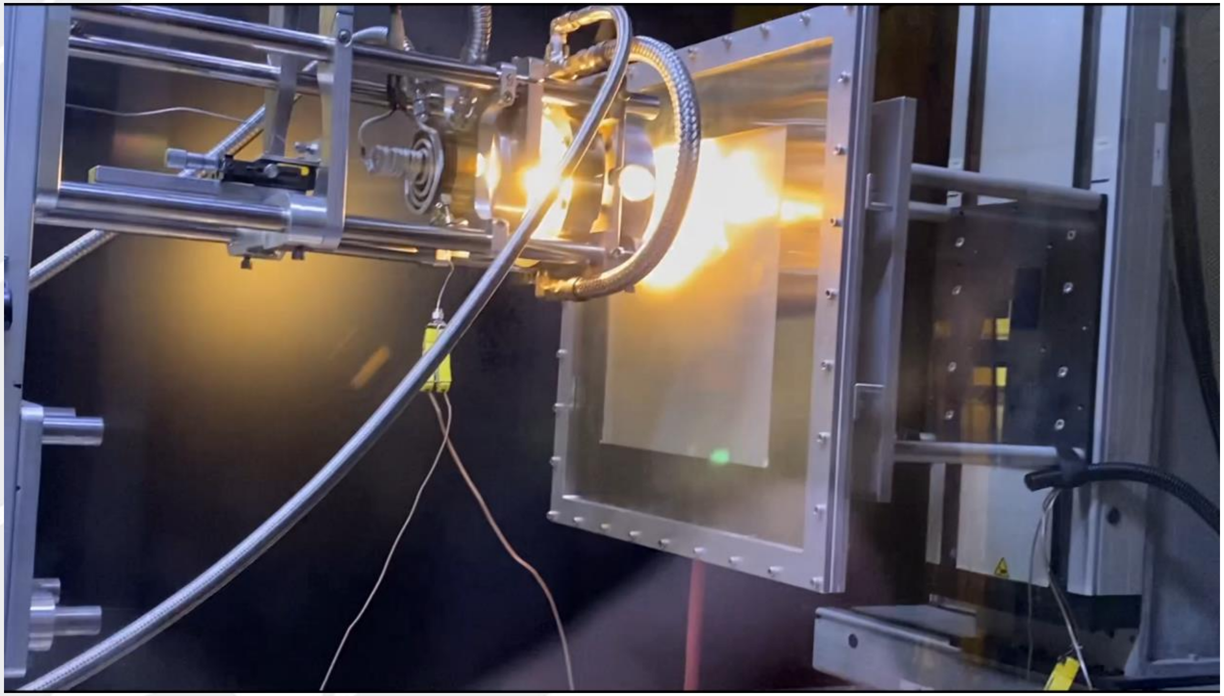
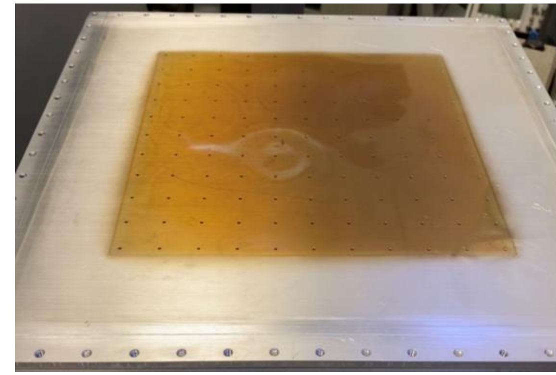
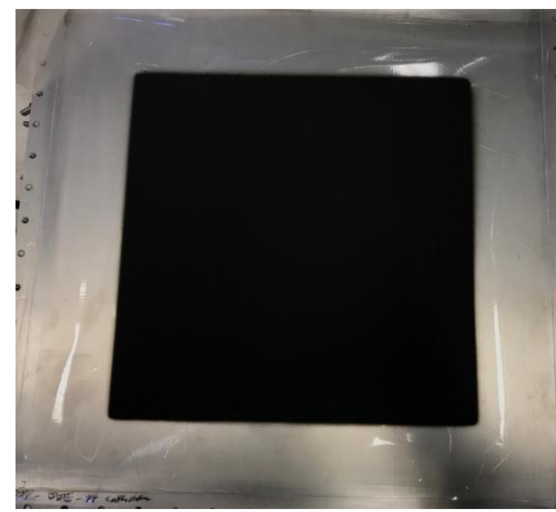
Initial Scale-Up RSDT Deposition Trials



680 cm^2 Pt RL deposited on Nafion 117



680 cm^2 Pt/C cathode catalyst layer deposited on Nafion 117



- Initial recombination layer and cathode RSDT trials have been completed at the 680 cm^2 area
- RSDT has been modified and verified to operate with desired membrane size
- Able to utilize deposition parameters used in 86 cm^2 samples without requiring a significant increase in deposition time
    - Despite 4x the enlarged deposited area the deposition time required was only increased by 66 %

Responses to Previous Year Reviewers' Comments

"This project was not reviewed last year."

Collaboration & Coordination

Partners	Project Roles	Collaborative Relationship
UCONN (University)	Project lead Management and coordination, catalysts and recombination layer design and development, in-situ catalysts synthesis by RSDT and direct CCMs fabrication, materials analysis and characterization	Bi-weekly conference calls Site visits as required to address development needs (5 site visits total): UConn at Proton – 3 visits Mainstream at UConn – 2 visits Technical progress reports discussions Planning research activities Monthly meetings /quarterly reports, discussions and coordination
NEL Hydrogen (Industry)	Sub MEA device design, single MEAs and short stacks testing and performance evaluation	
Mainstream Engineering (Industry)	Sub In-line quality control for MEA fabrication, device design for spectroscopic analysis	

Remaining Challenges and Barriers

- Scale up the RSDT manufacturing process and demonstrate capabilities for fabrication of large (680 cm^2) MEAs with industrial significance.
    - Demonstrate performance (H_2 crossover and I-V polarization) of MEAs with 680 cm^2 cell area.
    - Demonstrate stable performance and effective H_2 crossover reduction for over 1000 hours for 680 cm^2 cell area.
- Collect optical images on 680 cm^2 cells at real time and verify the thickness, composition, and catalyst loading of the deposited catalyst layers.
- Obtain and analyze in-situ Raman spectra from Pt and Ir nanoparticles formed in the RSDT flame.

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Proposed Future Work

Budget Period II:

- Scale-up the MEAs fabrication size from 86 to 680 cm^2, with catalysts loading of 0.2 mg_{Pt}/cm^2 and 0.2 - 0.3 mg_{Ir}/cm^2 at the cathode and anode, respectively.
- Determine the optimal Ir and Pt catalyst synthesis process by comparing the Raman spectra of IrO_x and Pt to cell performance.
- Collect data with installed in-line quality control system and optimize the thickness and catalyst loading. Confirm that the repeatability is with less than 10% standard deviation.
- Verify catalyst loading and thickness homogeneity with SEM, TEM, ICP analysis, and optical imaging.
- Test the 680 cm^2 MEAs at 1.8 A/cm^2 and demonstrate identical or better performance with the 86 cm^2 MEAs, and durability of over 1000 hours.
- Perform post test analysis of the MEAs by HRTEM, STEM, XRD, EDS, SEM, ICP, XPS, and XCT and identify the potential degradation mechanisms.

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

Scale-up fabrication of MEAs with in-line quality control

- Proton and UConn have an Intellectual Property Agreement which provides Proton with an option to an exclusive license in its field to any Project IP or UConn Background IP that may be necessary for the commercialization of its electrolyzers.

Summary

Objective:

Demonstrate the capabilities of the RSDT method for direct catalysts deposition and fabrication of large scale (680 cm^2) MEAs that meet the performance, manufacturing, and cost reduction targets.

For BP I (Jan. – Dec. 2019), all following objectives have been achieved for 86 cm^2 MEAs:

- ✓ Developed a recombination layer to decrease hydrogen permeation below 10 %LFL.
- ✓ Demonstrated performance on 86 cm^2 MEAs with ten times reduced catalyst loadings within 50 mV of baseline commercial electrodes at 1.8 A/cm^2.
- ✓ Demonstrated durability of the MEAs for over 1000 hours with less than 50 microvolts/hour degradation rate.
- ✓ Optimized RSDT parameters for fabrication of full 86 cm^2 MEA.

Approach:

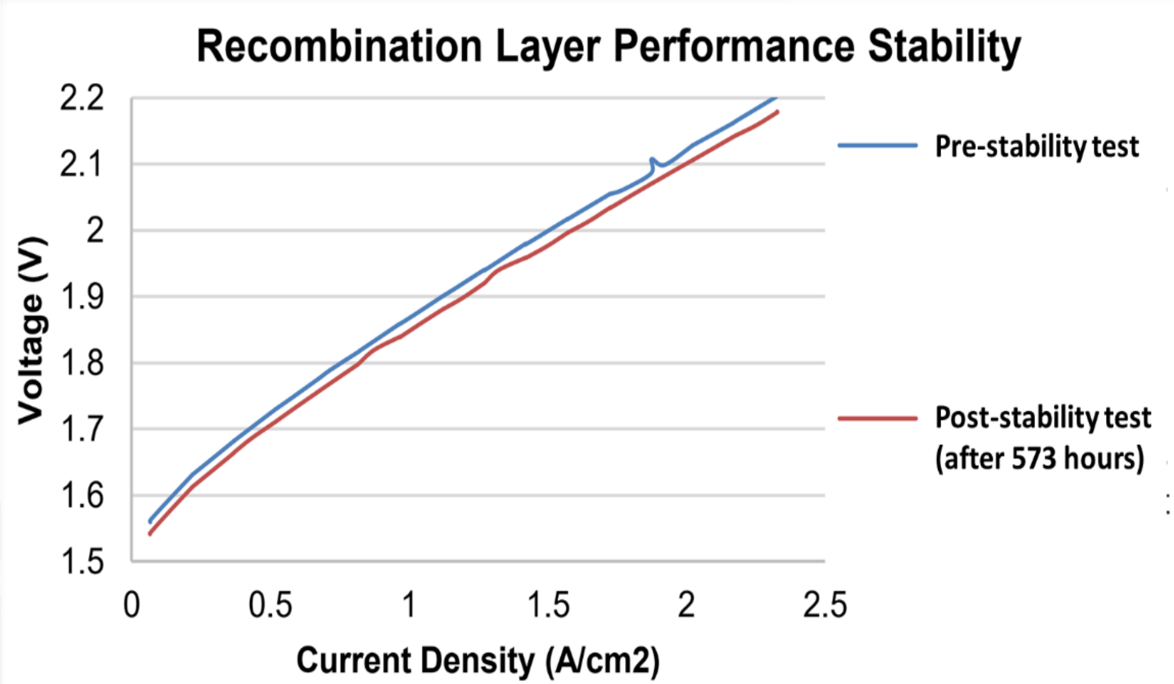
- Finalize MEA fabrication procedure for RSDT.
- Reduce hydrogen crossover with the design of the recombination layer.
- Examine in-situ MEA homogeneity and catalyst layer thickness with fixed-angle reflectance.
- Evaluate catalyst activity and MEA performance at 1.8 A cm^{-2}, 50 ^oC, and 400 psi differential pressure.

Accomplishments: All objectives of BP I have been achieved. Successfully met the BP I Go/No-go criteria. The MEA fully fabricated using RSDT process demonstrated >3000 hrs. of stable operation with negligible degradation of performance. The effectiveness of H_2 crossover reduction is maintained during long-term operation. Both Pt and Ir catalyst loadings are reduced by >10X in the RSDT MEA compared to commercial references.

Technical Back-Up Slides

Cell performance with MEAs incorporated with RSDT recombination layers

Cathode: commercial GDE, Pt loading 3 mg cm^{-2}, anode: commercial GDE, Ir loading, 3 mg cm^{-2}; Recombination layer: 1X Pt loading, Membrane: N117, 50 ^oC, 400 psi differential pressure; Active area: 86 cm^2.



- The recombination layer does not show adverse effect on the electrolyzer performance after long-term operation.

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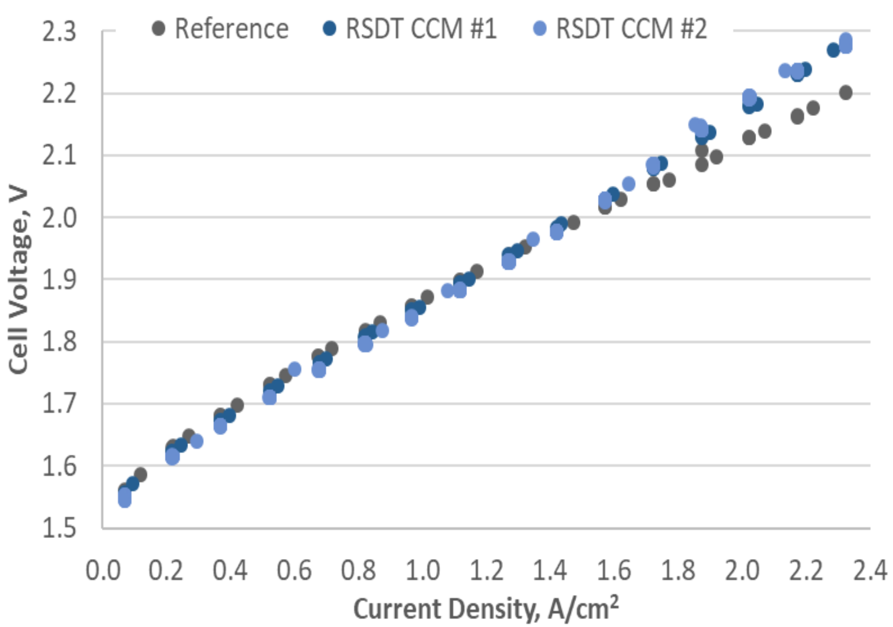
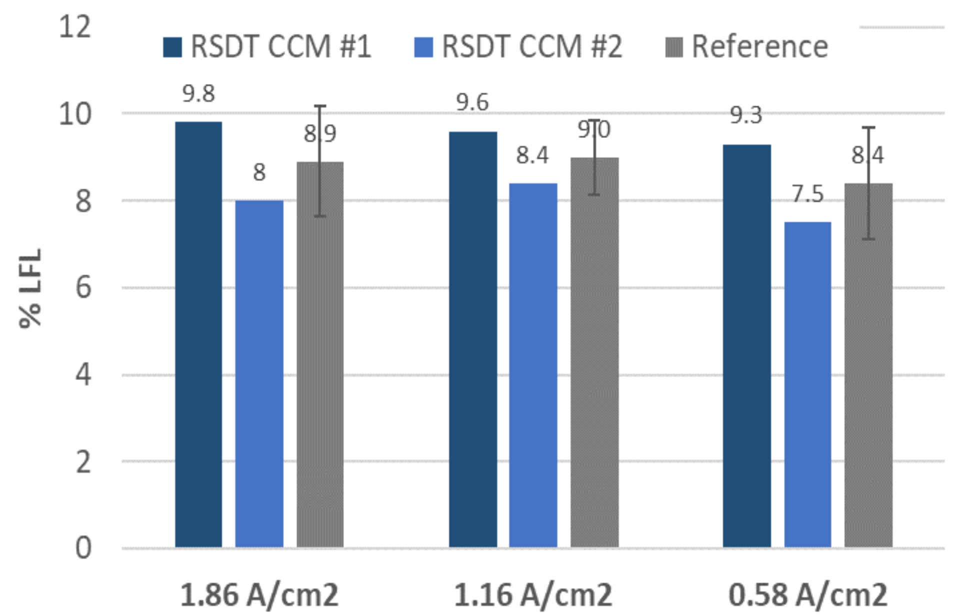
Performance of RSDT-fabricated MEAs

Reproducible initial performance and H_2 crossover reduction (MEA#1 and #2)

RSDT cathode: Pt/Vulcan XC-72R, 0.2 mg_{Pt} cm^{-2}, I/C ratio 0.15;RSDT anode, Ir loading, 0.3 mg cm^{-2}; RSDT recombination layer: 1X Pt loading, membrane: N117, 50 ^oC, 400 psi differential pressure; active area: 86 cm^2.





- The performance of MEAs fully fabricated with RSDT is reproducible and similar to Proton's commercial reference.
- The H_2 crossover is less than 10 %LFL and is comparable to Proton's commercial reference.
- Slightly higher cell voltage than reference at current >2.0 A/cm^2.

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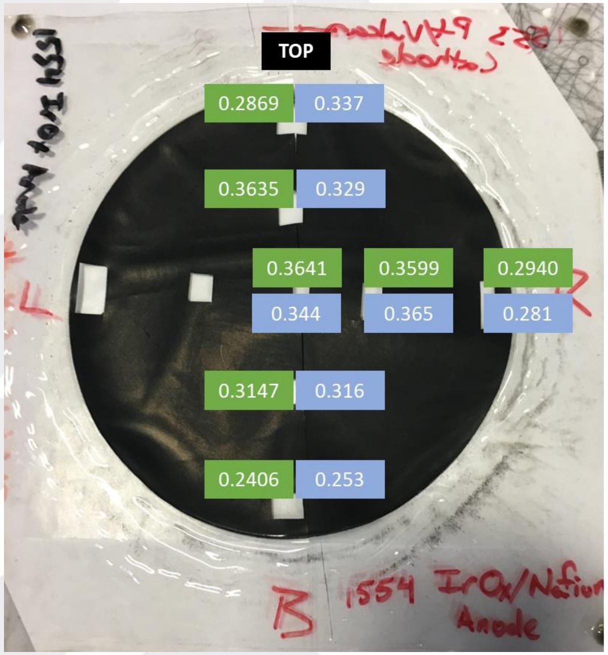
Distribution of catalyst loading at 86 cm^2

Iridium anode

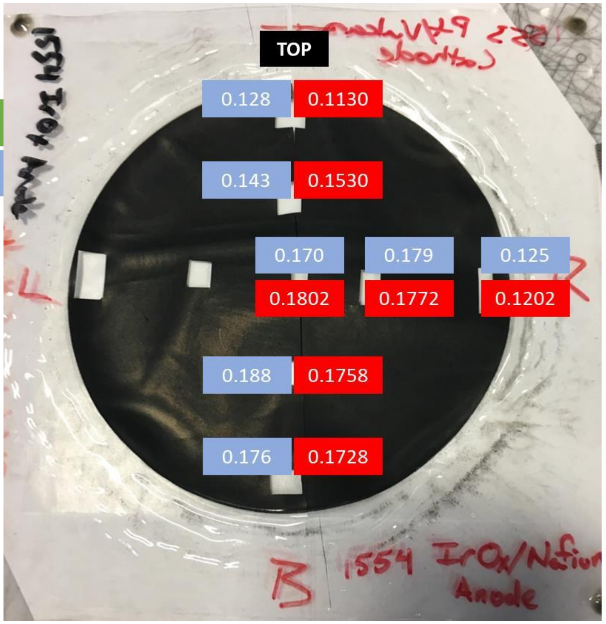


Unit: mg/cm^2

Anode/ICP

Mainstream

Platinum cathode



Unit: mg/cm^2

Cathode/ICP

Mainstream

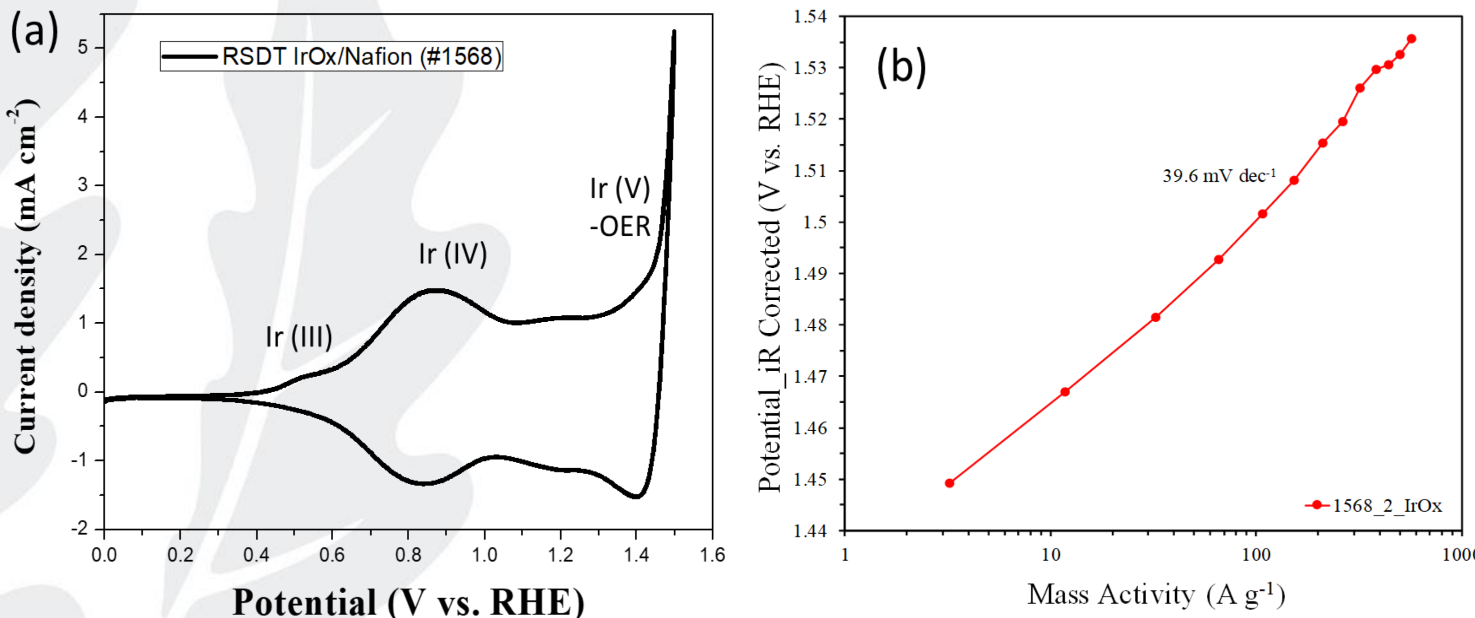
- Comparison of ICP analysis and optical reflectance measurements (at Mainstream) of catalyst loadings. These data are used to plot the figures (optical vs ICP) in slide 10.

Technical Back-Up

Evaluation of OER activity for RSDT-synthesized IrO_x catalyst

Electrochemical measurement in RDE

CV (a) and OER Tafel plot (b) for RSDT-fabricated IrO_x/Nafion catalyst. CVs were recorded at 20 mV/s, 25 ºC, in N_2-purged 0.1M $HClO_4$ electrolyte and 10 repeatable cycles are shown. The IR-corrected polarization curves were recorded at 10 mV/s, 25 ºC, in N_2-purged 0.1M $HClO_4$ electrolyte. EIS were measured at each potential step to obtain the ohmic resistance



- The CV (a) shows three pair of redox peaks of Ir oxides, in agreement with our previous published work [1]
- The Tafel slope agree with proposed OER mechanism in the literature.
- OER mass activity reached 320 A/g_{IrO2} at 1.525 V which agree with our published work [1] and is higher than state-of-the-art IrO_x synthesized from wet chemistry method [2]

[1] Yu, H., et al. Appl. Catal. B.239 (2018) 133–146

[2] Abbott, D.F., et al. Chem. Mater. 28 (2016) 6591–6604

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