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Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique

2014 DOE Hydrogen and Fuel Cells Program Review

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FC111

This presentation does not contain any proprietary, confidential, or otherwise restricted information.

Overview

Timeline

Project start date: 10/1/2013
Project end date: 9/30/2014

Budget

Total project funding: $175k
NREL (Electrochemical Charac. Lab):75k
ANL (Energy Conversion and Storage):50k
ANL (Hydrogen and Fuel Cell Materials):50k
Total funding planned for FY14: $175k

Barriers

- Inconsistencies in reported ORR catalyst activity measurements using RDE
- Lack of standard Pt/C catalysts and established benchmark activity values
- Lack of a standard RDE measurement protocol
- Lack of standard electrode/ink prep

Partners

- ANL: Vojislav Stamenkovic, co-PI
- ANL: Deborah Myers, co-PI
- Johnson Matthey (JM)
- Tanaka Kikinzoku Kogyo (TKK)
- Umicore

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Relevance

Objectives

- **To aid DOE in meeting goals for catalyst performance and durability by:-**
  - Establishing protocols and best practices for ink dispersion/film deposition/drying for rotating disk electrode (RDE) measurements to allow for more precise and reproducible data and reliable comparisons to be made by electrocatalyst development groups when evaluating novel synthesized catalysts in small quantities.

Background

Several groups over the last few years reported discrepancies in activity values reported between research groups and also improvements in technique that allowed higher and more reproducible activity.
*CWG and DWG Me*etings, Co-Chairs: Piotr Zelenay, Nancy Garland and Deborah Myers, Rod Borup, Honolulu, Hawaii, 2012;
ECS, HNL meeting S. Kocha et al. 2012, ECS SF meeting, 2013; Garsany et al. & ECS SF meeting, 2013; Shinozaki et al. 2013.

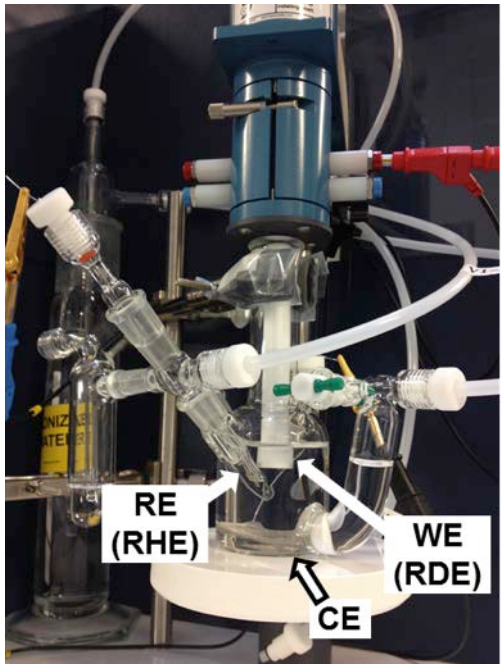
DOE worked with NREL and ANL to issue a Request for Information (RFI) on best practices for RDE measurements for ORR activity

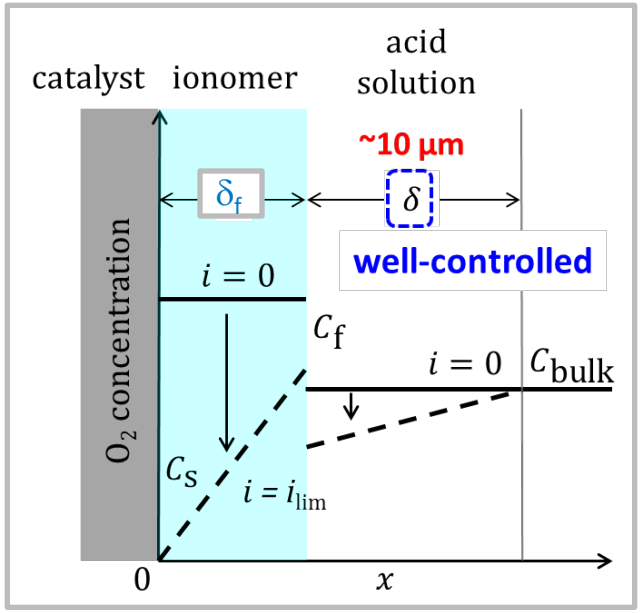
DOE organized a webinar on RDE. Shyam S. Kocha, Yannick Garsany, Deborah Myers, Chair: Dimitrios Papageorgopoulos, 'Testing Oxygen Reduction Reaction Activity with the Rotating Disc Electrode Technique', March 12, 2013.
http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/webinarslides_rde_technique_031213.pdf

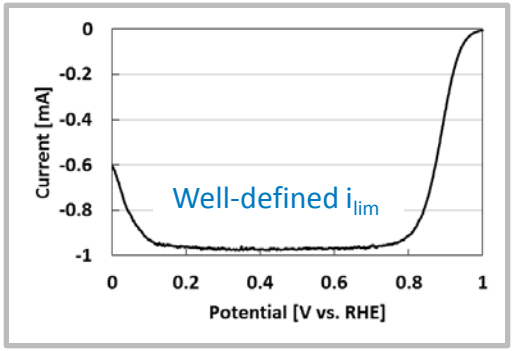
DOE funded AOPs for NREL and ANL to work on this project

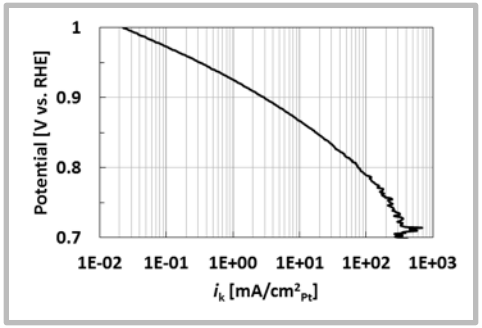
DOE organized the Catalysis Working Group (CWG) meeting and Durability Working Group (DWG) meeting at NREL/DOE Field Office, December 2013, with one of the objectives being the discussion of responses to the RDE RFI.

TF-RDE Technique









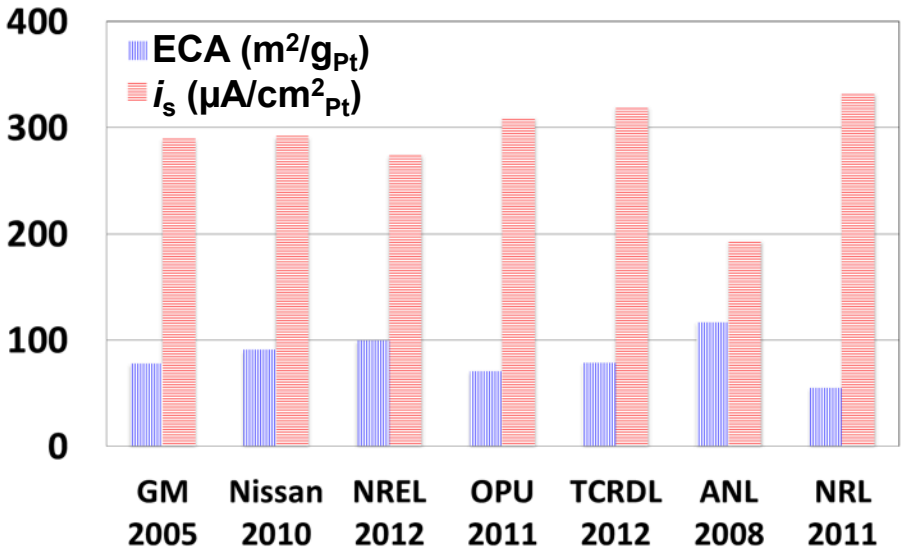
- —Well-defined i_{lim}
- —Peroxide from RRDE
- —Commercially available
- —Small quantities of catalysts
- —High throughput
- —Reasonable Cost

A solid benchmark accompanied by best practice methodology & standard test protocol essential for comparison to novel catalysts and between groups

TF-RDE was selected as the technique for screening PEMFC catalysts.

Literature Review

'Measured' Activity



(GM) TKK 46 wt% Pt/HSC, 60°C, 20 mV/s, no iR comp, no b.g. correc

(Nissan) TKK 46 wt% Pt/HSC, 30°C, 10 mV/s, no iR comp, b.g. correc

(NREL) TKK 46 wt% Pt/HSC, 25°C, 20 mV/s, iR comp, no b.g. correc

(ANL) TKK 20 wt% Pt/C, 60°C, 20 mV/s, no iR comp, no b.g. correc

(NRL) 19.7 wt% Pt/V, 30°C, 20 mV/s, no iR comp, no b.g. correc

(OPU) TKK 46 wt% Pt/HSC, 25°C, 10 mV/s, no iR comp, no b.g. correc

(TCRDL) TKK 46 wt% Pt/HSC, 30°C, 10 mV/s, no iR comp, b.g. correc

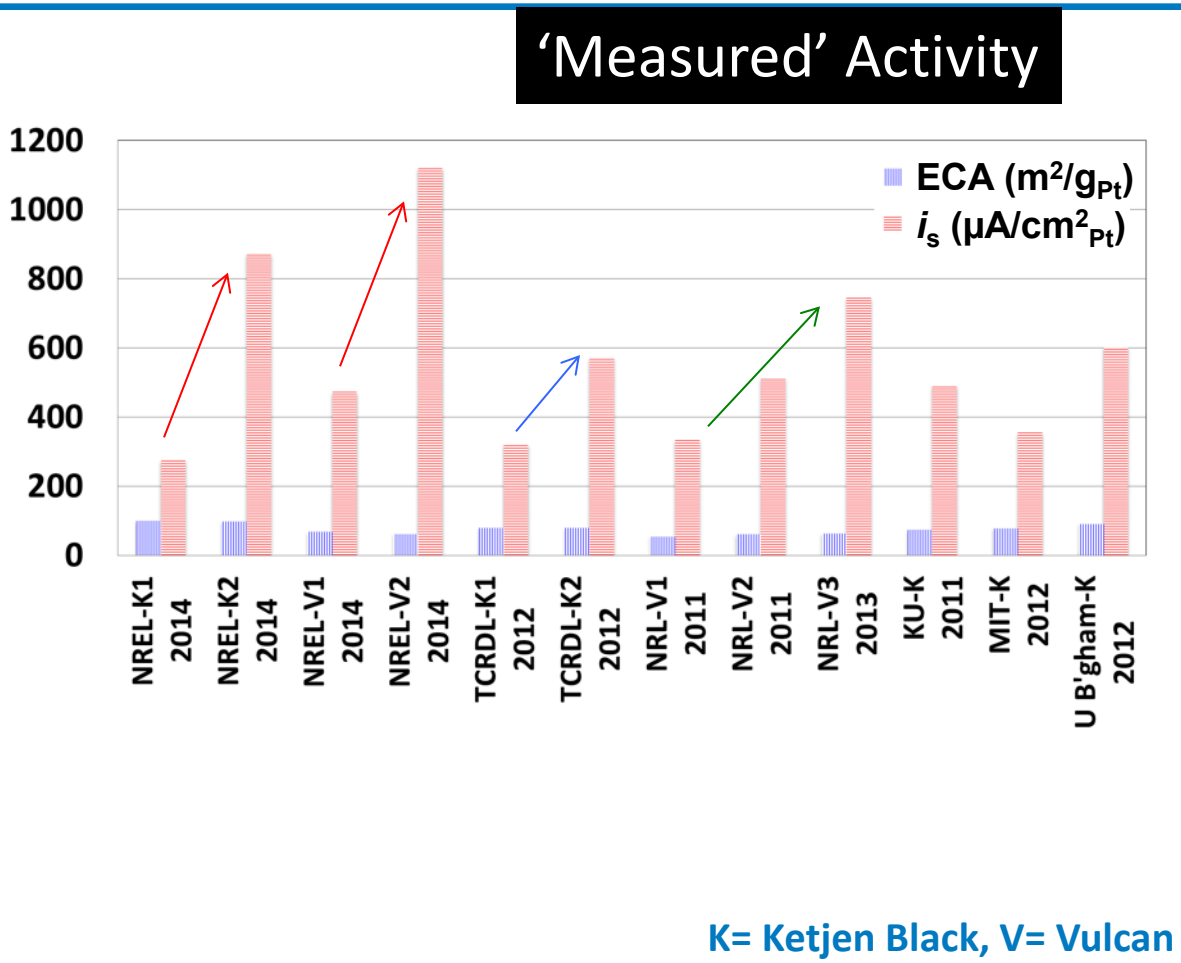
Parameters/phenomena affecting measured activity

Electrocatalyst; Contaminants; Test Protocol; Corrections (iR, b.g.); Ink formulation, composition & dispersion; Film-uniformity; loading/thickness

R_{el}: electronic
R_{H+}: protonic
O_2 Diffusion
SO_3H Adsorption

Even with thick, non-uniform films—comparable activity obtainable.

Recent Advancements–Literature



K= Ketjen Black, V= Vulcan

(NREL-K1&V1) TKK 46 wt% Pt/HSC, 25°C, 20 mV/s, iR comp, no b.g. corr. (Nafion®-based coffee ring)
(NREL-K2&V2) TKK 46 wt% Pt/HSC, 25°C, 20 mV/s, iR comp, b.g. corr. (Nafion®-free thin-uniform)
(TCRDL-K1&2) TKK 46 wt% Pt/HSC, 30°C, 20 mV/s, no iR comp, b.g. corr. (K1: Nafion®-based coffee ring, K2: Nafion®-based thin-uniform)
(NRL-V1&2) 19.7 wt% Pt/V, 30°C, 20 mV/s, no iR comp, b.g. corr. (V1: Nafion®-based coffee ring, V2: Nafion®-based uniform (rotational))
(NRL-V3) 19.7 wt% Pt/V, 30°C, 20 mV/s, iR comp, b.g. corr. (V3: Nafion®-based uniform (rotational) same as V2)
(KU-K) TKK 46 wt% Pt/HSC, 25°C, 50 mV/s, iR comp, b.g. corr. (Nafion®-free)
(MIT-K) TKK 46 wt% Pt/HSC, 25°C, 10 mV/s, no iR comp, b.g. corr. (Nafion®-free)
(U B'gham-K) TKK 46 wt% Pt/HSC, 25°C, 25 mV/s, iR comp, b.g. corr. (Nafion®-free rotational dry)

Minimizing— R_{el}: electronic; R_{H+}: protonic; O_2 diffusion, & SO_3H adsorption losses in the RDE catalyst layer can lead to significantly higher 'measured activity'

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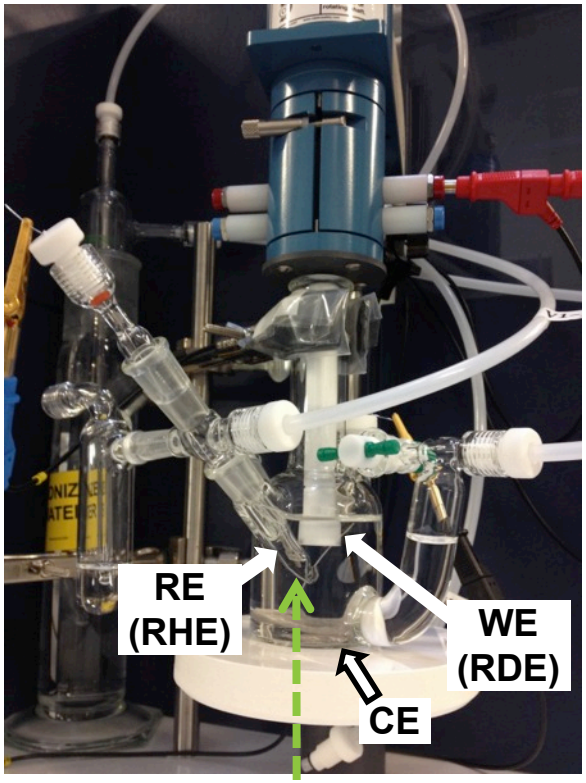
Approach

Approach

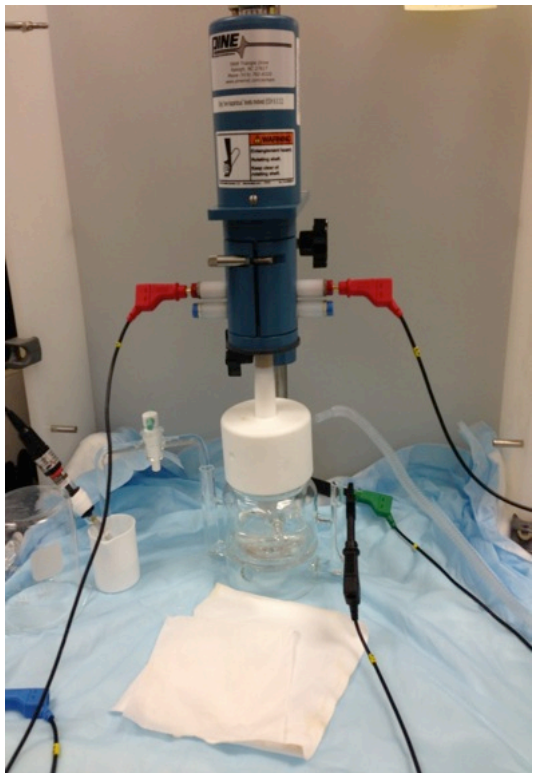
- Identify 2–3 commercially obtainable Pt/C electrocatalysts
- Select suitable protocols and ink dispersion/film deposition methods (based on accumulated data)
- Utilize identical protocols and ink formulation/film deposition methods and evaluate the electrocatalysts in 3 laboratories. (different electrochemical cell glassware)
- Obtain electrochemical activity measurements that have a high degree of statistical reproducibility
- Verify the results between laboratories.

Electrochemical Cell System



RHE, No Salt Bridge

Electrochemical Conversion Laboratory, NREL



SCE, Salt Bridge

Energy Conversion and Storage, ANL-VS

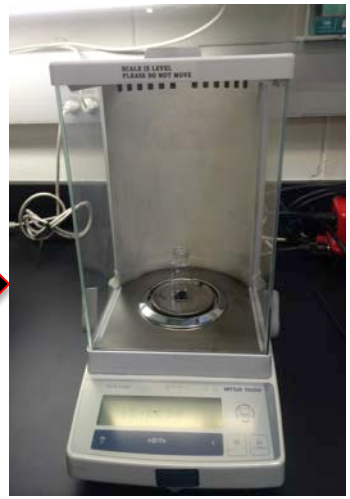
Hg/Hg_2SO_4, Salt Bridge

Hydrogen and Fuel Cell Materials Group, ANL–DM

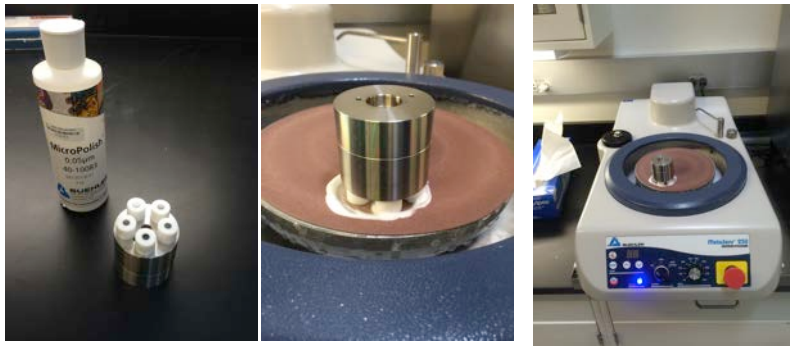
Cell glassware, reference, potentiostats are different in the 3 labs.

GC Preparation and Catalyst Ink Formulation

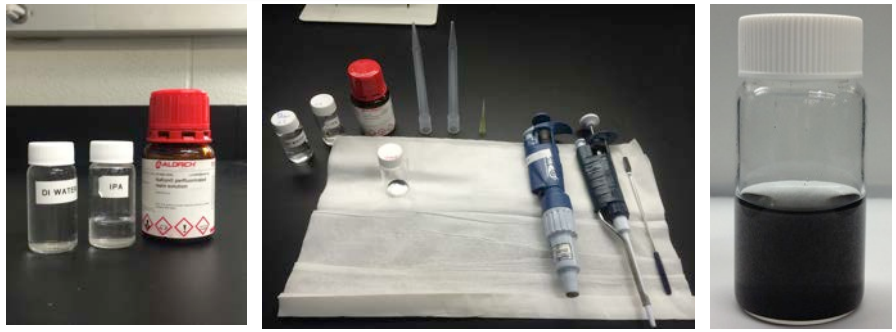
Catalyst



Balance



Polish GC

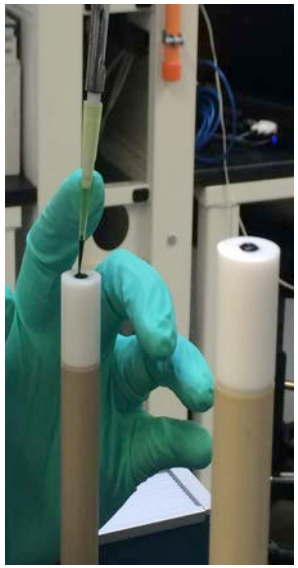


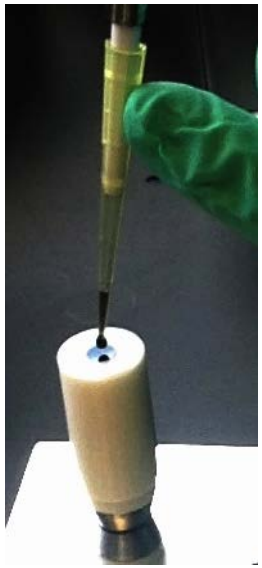
Prepare

TF-RDE: Film Deposition/Drying

Sonicator

Ink

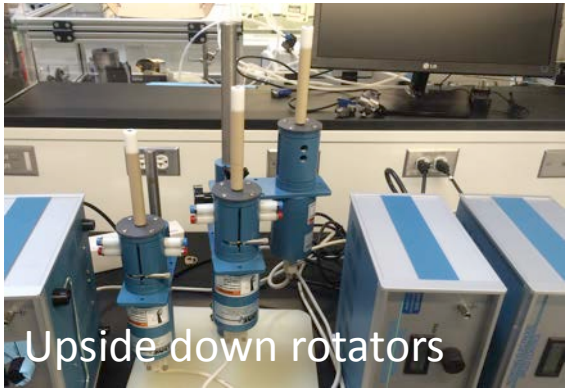




Deposit (5–10 µL)

Stationary

Oven/40°C/ Air Dry



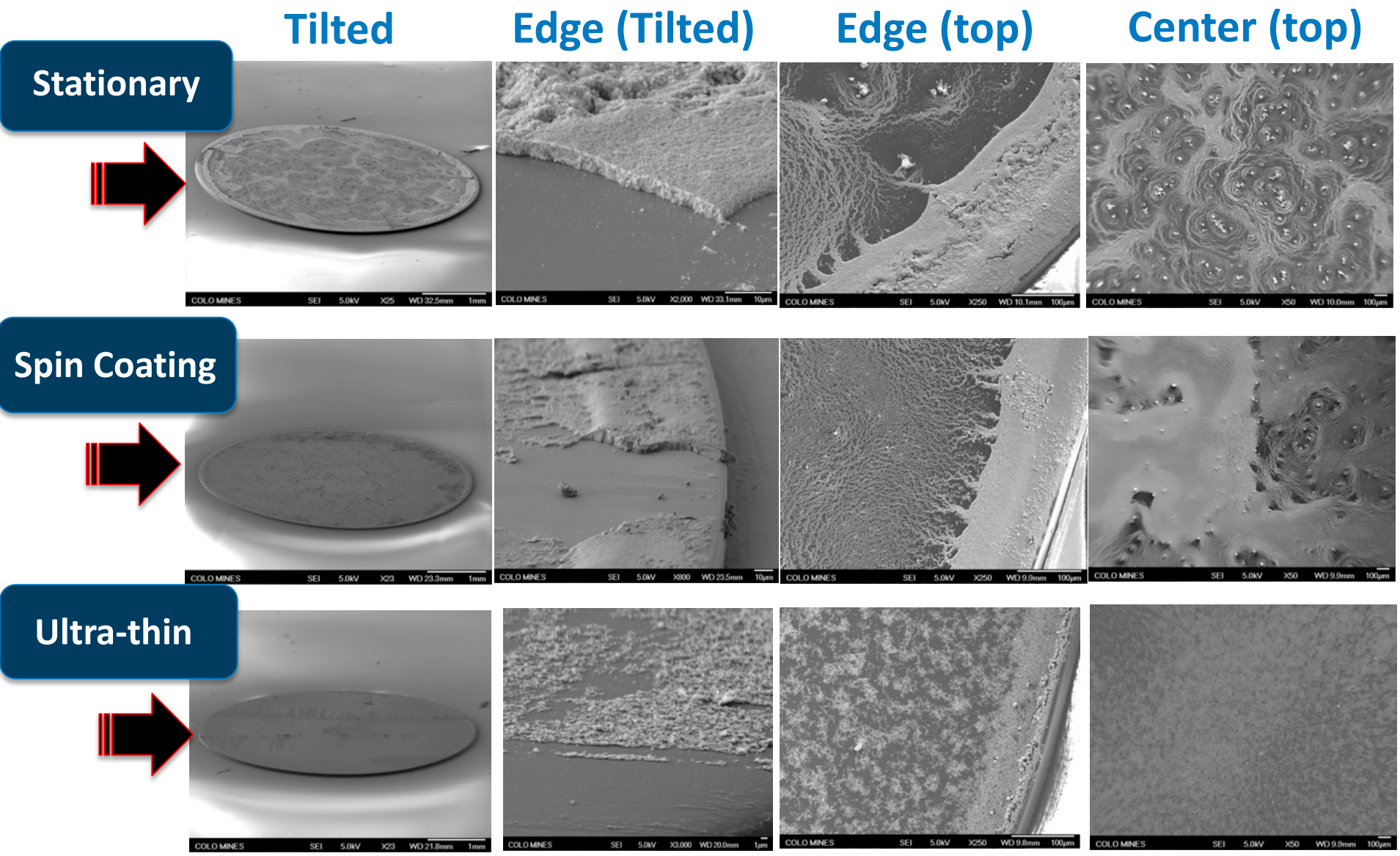
Spin Coating

Spin Coat/ Air Dry

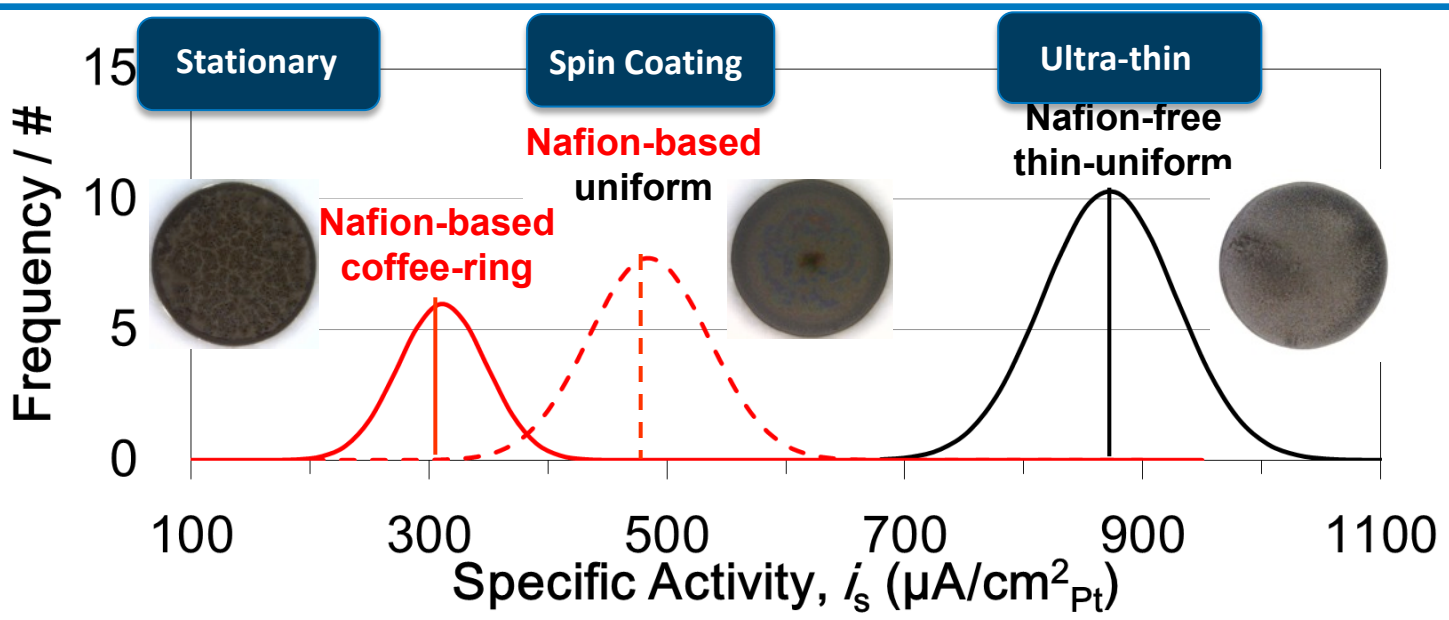
Ultra-thin

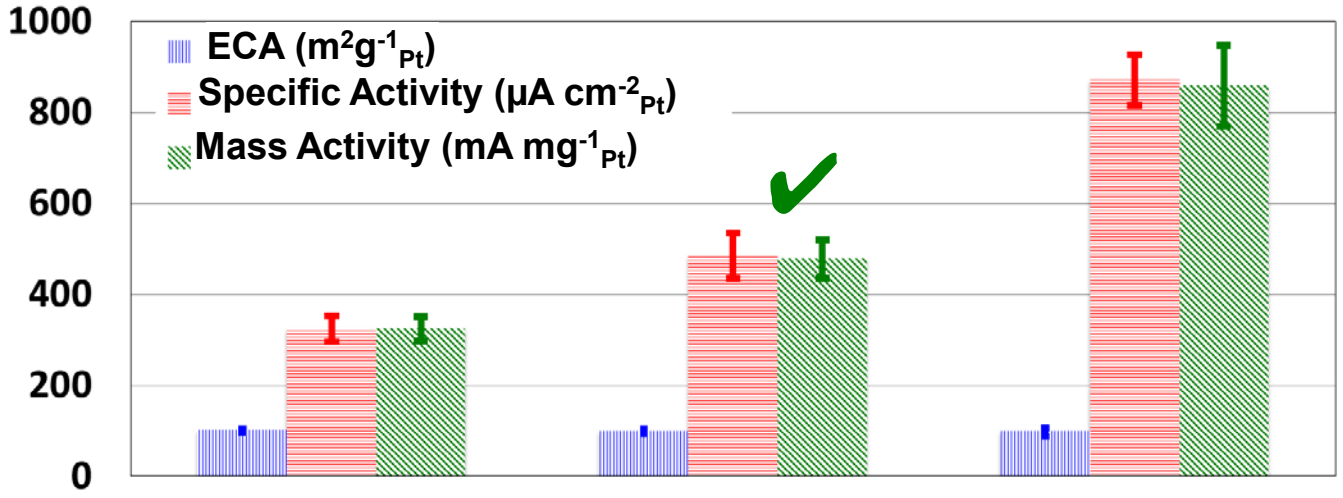
Oven/40°C/ IPA Dry

SEM: TF-RDE (TKK 46.4 wt% Pt/C)



Impact of Method (TKK 46.4 wt% Pt/C)





Spin coating selected since it is robust & not sensitive to operator skill.

Selection of Method (46.4 wt% TKK Pt/C)

Stationary

Thick, wide coffee ring

Non-uniform

Sensitive to operator skill

Typical method/values obtained in literature; **lower** activity values

SA ± 12% $\mu A/cm^2_{Pt}$

MA ± 11% mA/mg_{Pt}

28 samples

Spin Coating ✔

Moderate wide coffee ring

Moderately uniform

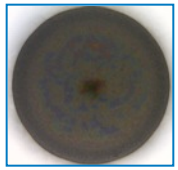
Less Sensitive to Pipetting/drying/operator skill

More recent method; **"Garsany Spin Coating Technique" moderately high** activity values

SA ± 10% $\mu A/cm^2_{Pt}$

MA ± 9% mA/mg_{Pt}

49 samples



Ultra-thin

Narrow coffee ring

Extremely uniform & thin

Sensitive to RH, operator skill

Very recently reported method–**highest measured activity** at this time.

SA ± 6% $\mu A/cm^2_{Pt}$

MA ± 10% mA/mg_{Pt}

58 samples (TKK)

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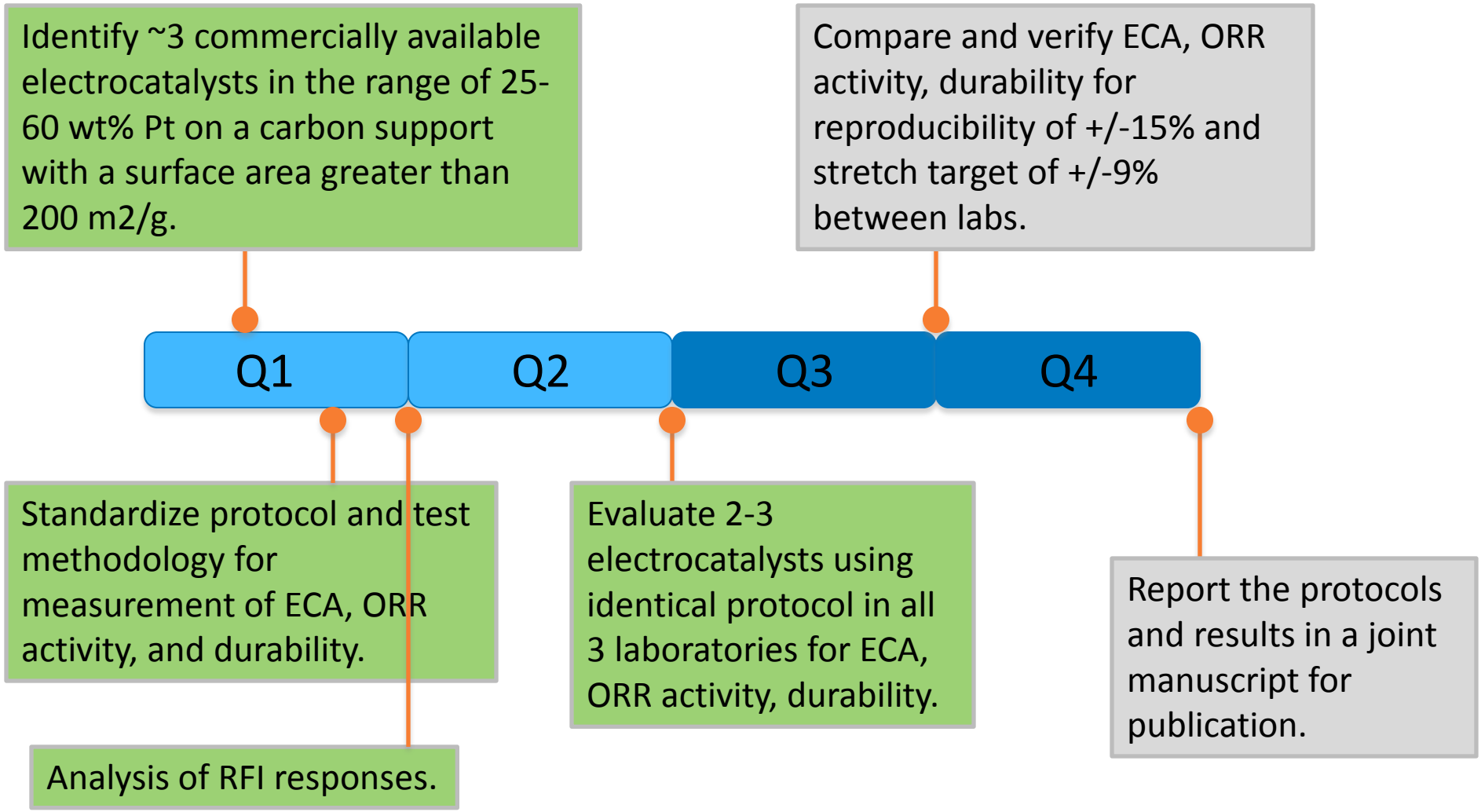
Accomplishments & Progress

Milestones (FY14)



Milestones till Q2 accomplished as per schedule.

Summary RDE Test Protocol/Expt. Conditions

Electrolyte: 0.1 M $HClO_4$

Cell Temperature: Room Temperature

Measurement Protocols

1. **Break-in:** 0.025 – 1.2 V, 0.5 V/s, 100 cycles, N_2
2. **CV:** 0.025 – 1.0 V, 0.02 V/s, 3 cycles, N_2
3. **IV:** –0.01 → 1.0 V, 0.02 V/s, 1600 rpm, O_2

Corrections

1. iR compensation
2. Background Correction
3. Limiting current corrected to 100 kPa;
4. Kinetic currents corrected to 100 kPa using total reaction order for ORR of 0.85.

Example Ink Formulation

(for 46.5 wt% Pt/C)

Pt/C : 7.6 mg

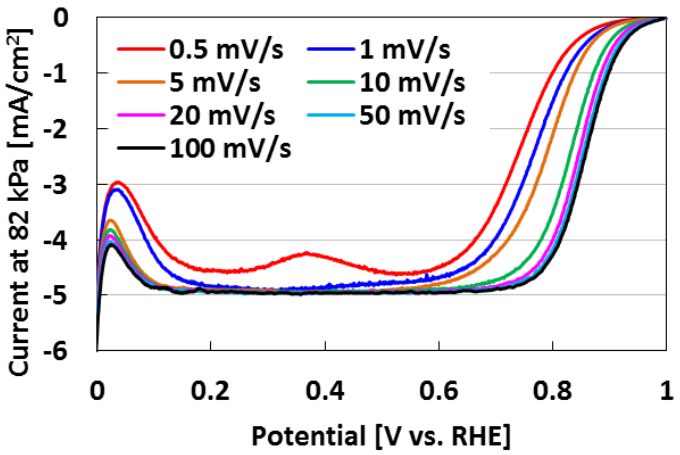
D.I. Water:7.6 ml

IPA: 2.4 ml

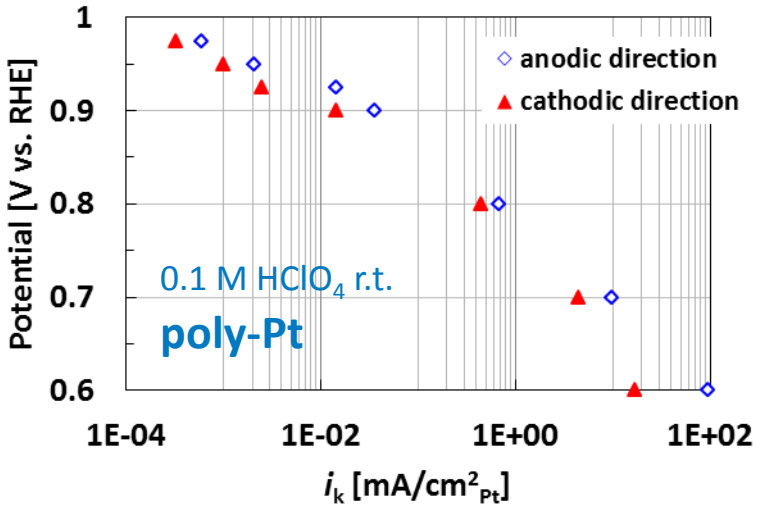
Sonication: Bath, ice, 20 min

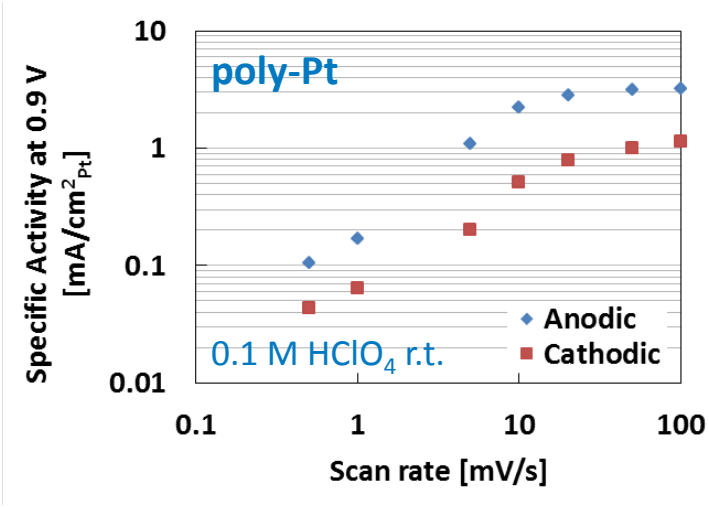
Spin Coating: 700 rpm, ~ 15 min

Choice of Protocol : Example–Scan Rate



15 min/point



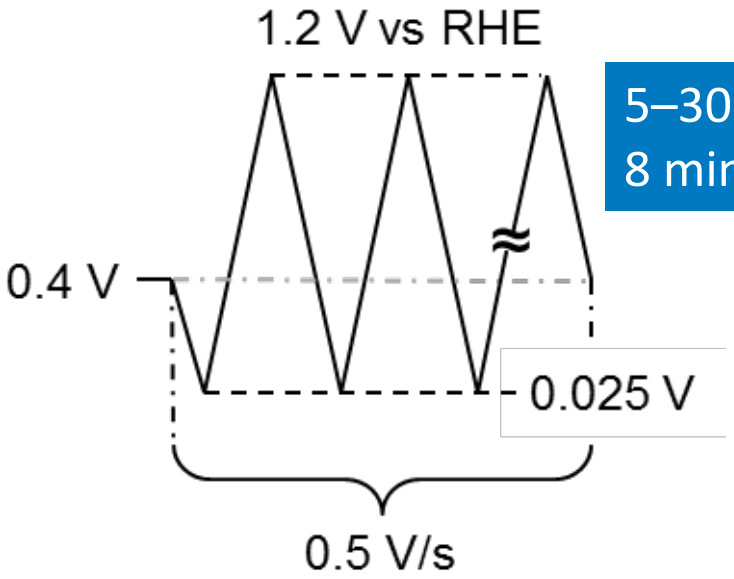


- Time required per experiment
- Magnitude of b.g correction
- Reproducibility

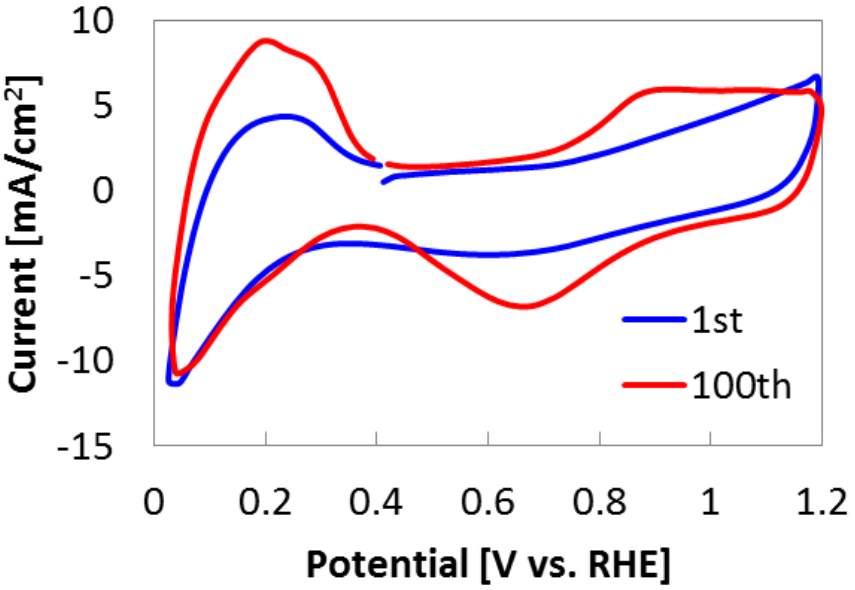
Impact of voltage range and scan direction also studied.

Protocol selected after considerable data acquisition and analysis.

Protocol: Break-in/Conditioning



5–30 min purge
8 min data

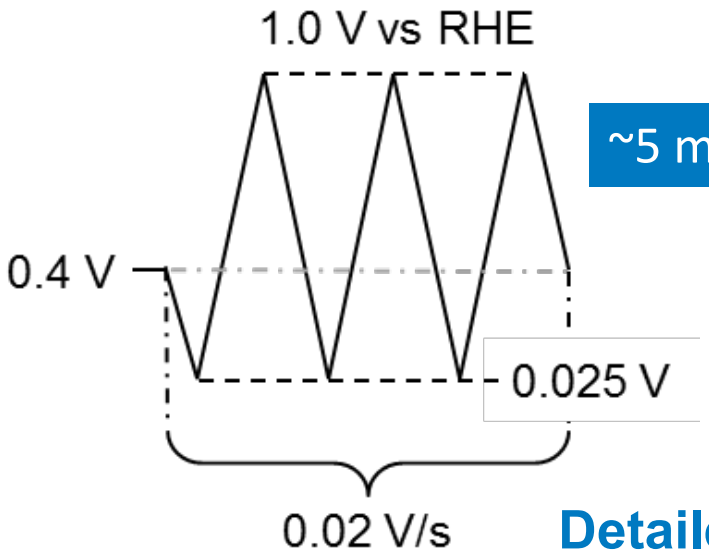


Detailed Conditions

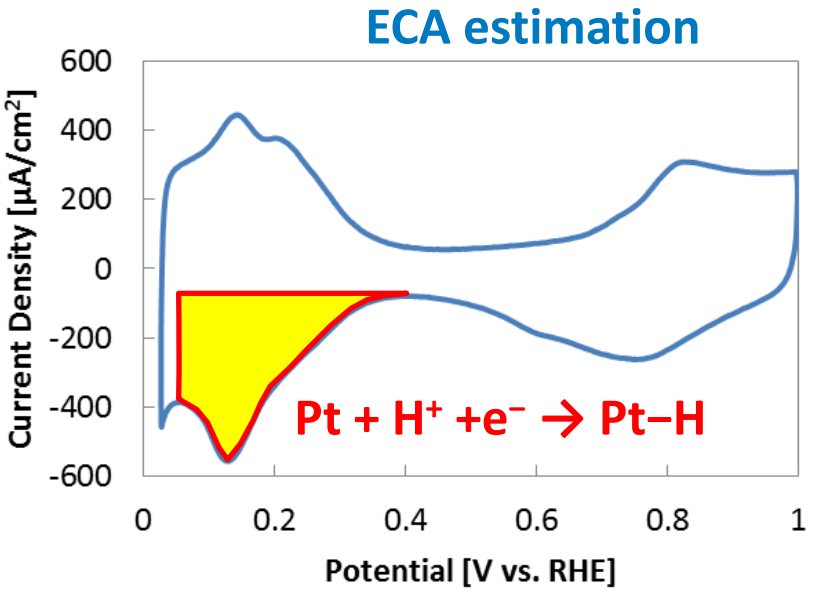
Gas	N_2
Temperature	r.t.
Rotation Rate [rpm]	2500
Potential Range [V vs. RHE]	0.025–1.2
Scan Rate [V/s]	0.5
Potential Cycle Number	50–100

Break-in cycles necessary to hit peak ECA and catalyst activity.

Protocol: CV under N_2



~5 min data

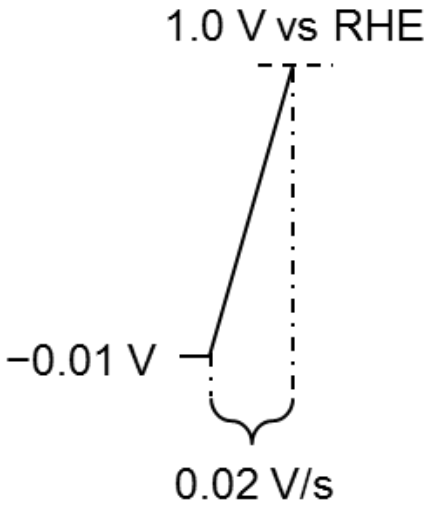


Detailed Conditions

Gas	N_2
Temperature	r.t.
Rotation Rate [rpm]	0
Potential Range [V vs. RHE]	0.025–1.0
Scan Rate [V/s]	0.02
Potential Cycle Number	3
Scan type	Linear (Analog)
ECA Estimation Method	H_{ads} charge

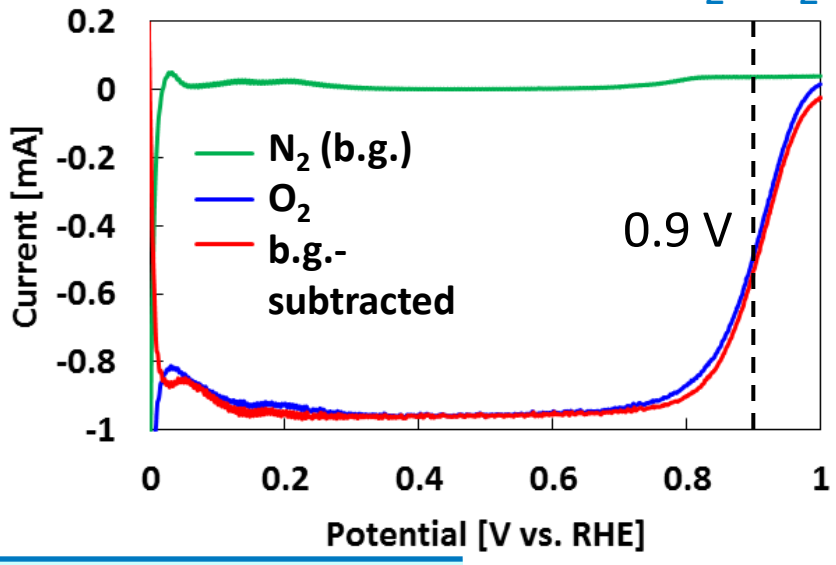
HUPD area from cyclic voltammogram used to determine ECA.

Protocol: ORR Activity Measurement



5–30 min purge
1 min data

(LSV under N_2, O_2)



Detailed Conditions

Gas	N_2 or O_2
Temperature	r.t.
Rotation Rate [rpm]	1600
Potential Range [V vs. RHE]	−0.01 to 1.0 (anodic)
Scan Rate [V/s]	0.02
R_{sol} measurement method	i-interrupter or EIS (HFR)
iR compensation	applied during measurement
Background Subtraction	LSV (O_2)−LSV (N_2)

0.90 V vs. RHE, 25°C, 100 kPa, 1600 rpm, O_2 saturated 0.1 M $HClO_4$.

Electrocatalyst Selection

1. Pine Instruments

Poly-Pt disk
Dia 5 mm; 0.196 cm^2
Thickness: 4 mm
Roughness: ~1.1–1.3

2. Tanaka (TKK)

TEC10E50E; Pt wt%: 46.4
Support: Carbon Black
TEM average particle size: ~2.5 nm (samples from 3 catalyst batches evaluated)

3. Johnson Matthey (JM)

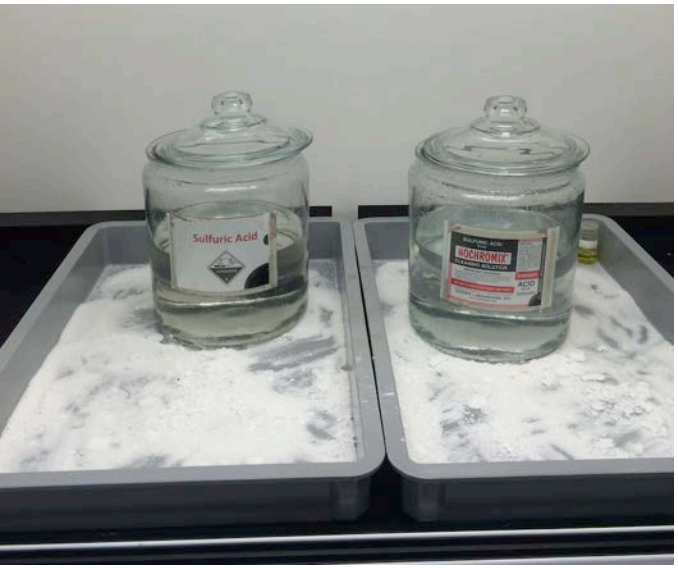
Pt wt%: 37.6
Support Ketjen EC 300J
CO Chemisorption area: 81 m^2/g_{Pt}
XRD crystallite size: <2 nm

4. Umicore

Elyst Pt50 0550; Pt wt%: 47.2
Support: Carbon Black
XRD crystallite size: ~4.9 nm
BET-surface: 365 m^2/g_{Pt}

Manufacturer specifications for electrocatalysts under study.

Cell Cleanliness & Perchloric Acid Source



Concentrated Acid Soak

Boiling in DI water/change water x6

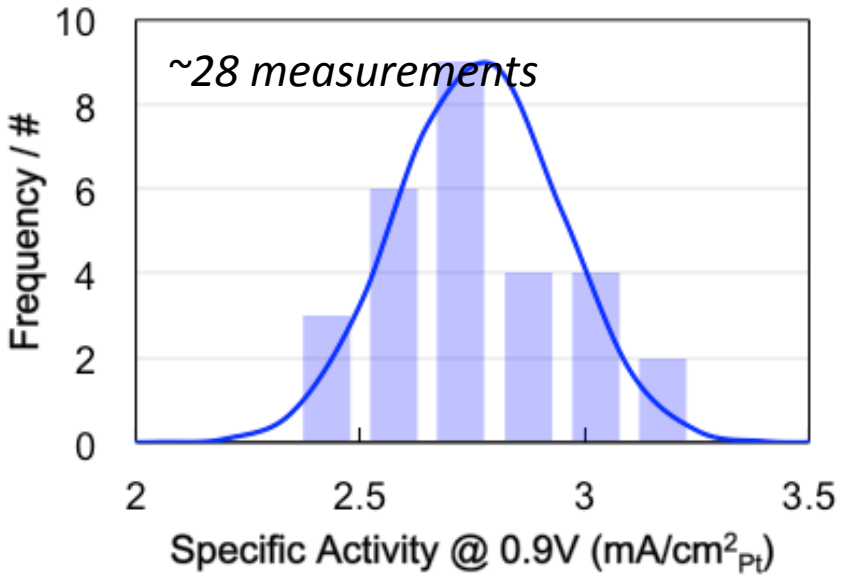
Sources of Perchloric Acid

Veritas® Doubly Distilled (GFS chemicals) ✔	✔
Omni Trace Ultra (EMD Millipore)	
J.T. Baker® ULTREX II Ultrapure (AVANTOR)	
TraceSELECT® (Sigma-Aldrich)	
Suprapur® (Merck)	
Superior ACS (GFS chemicals) ✔	
trace metal basis (Sigma-Aldrich)	✗
ACS (Sigma-Aldrich)	

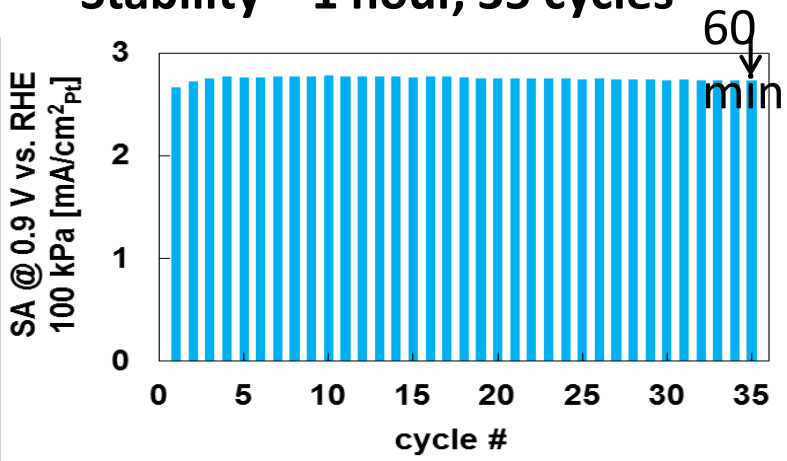
Rigorous cleaning of glassware and choice of perchloric acid is critical.

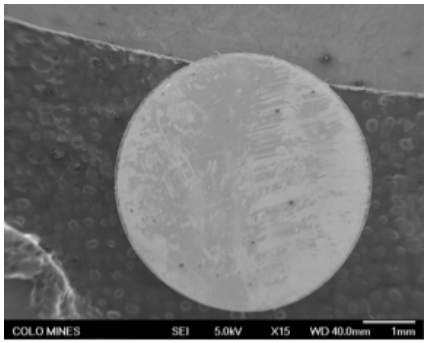
Poly-Pt: A Measure of Impurity Levels

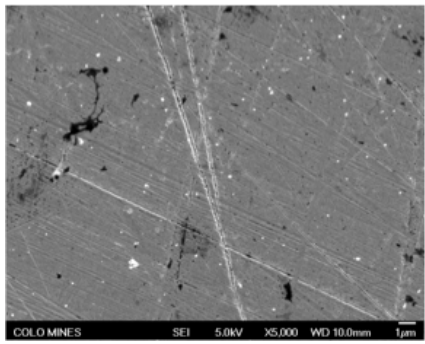
Sp. Activity = 2.8 ± 0.2 mA/cm$^2_{Pt}$



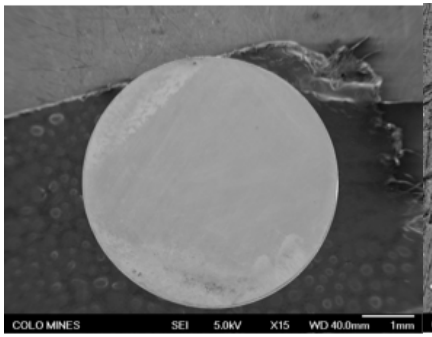
Stability ~ 1 hour, 35 cycles

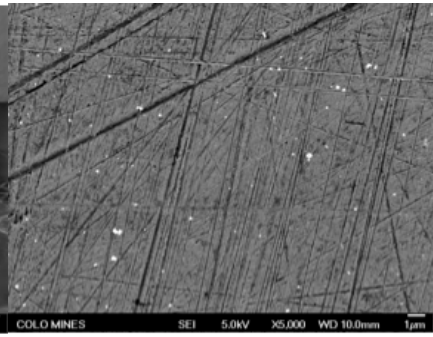






New unused poly-Pt disk

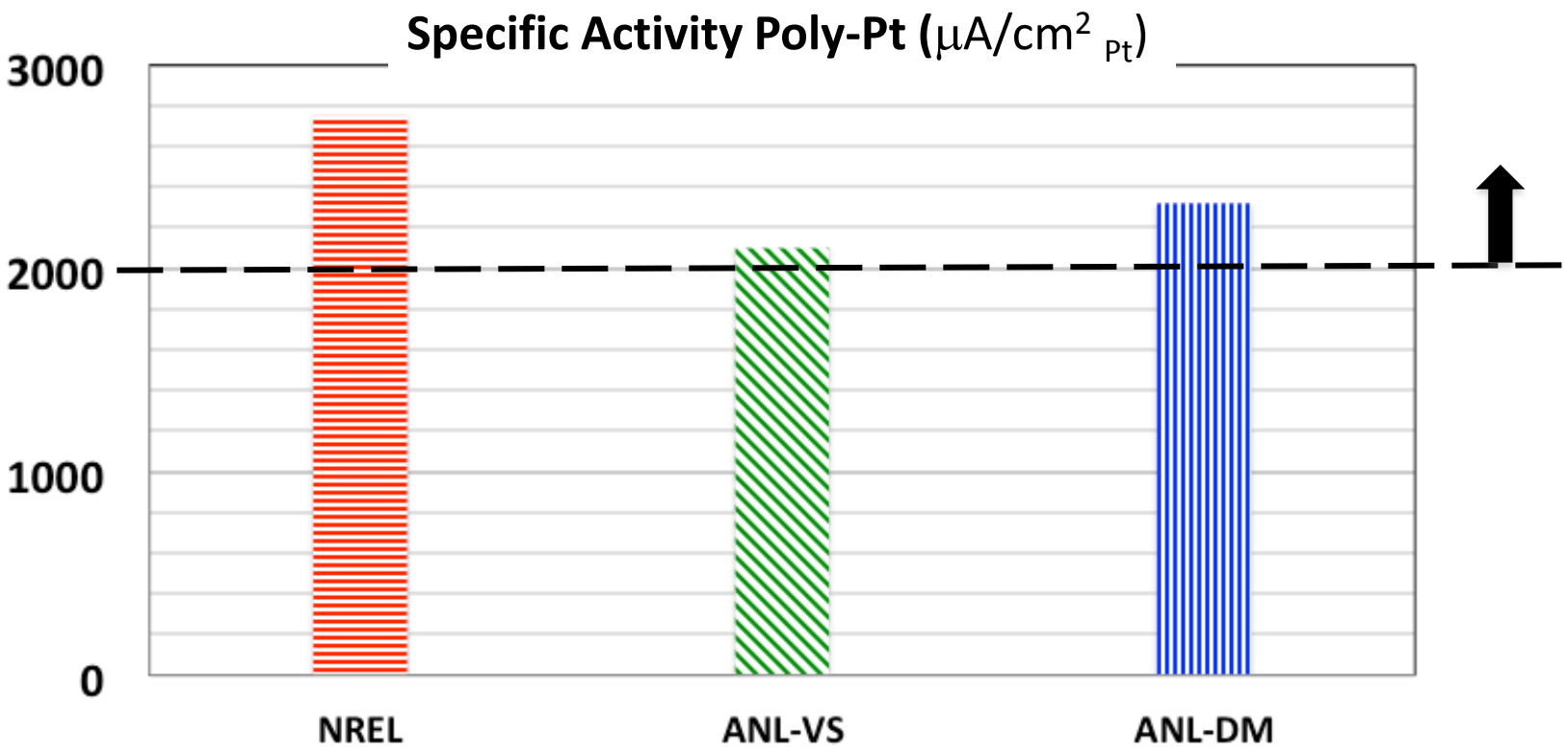




Used, polished poly-Pt disk

Even new unused poly-Pt electrodes exhibit significant surface roughness (SEM)

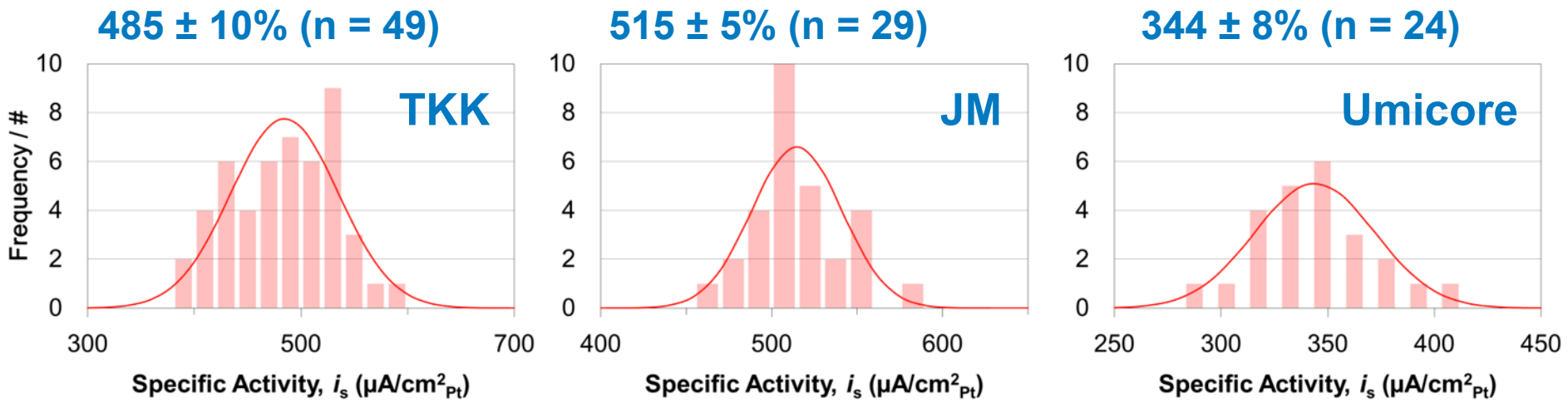
Comparisons Between Labs

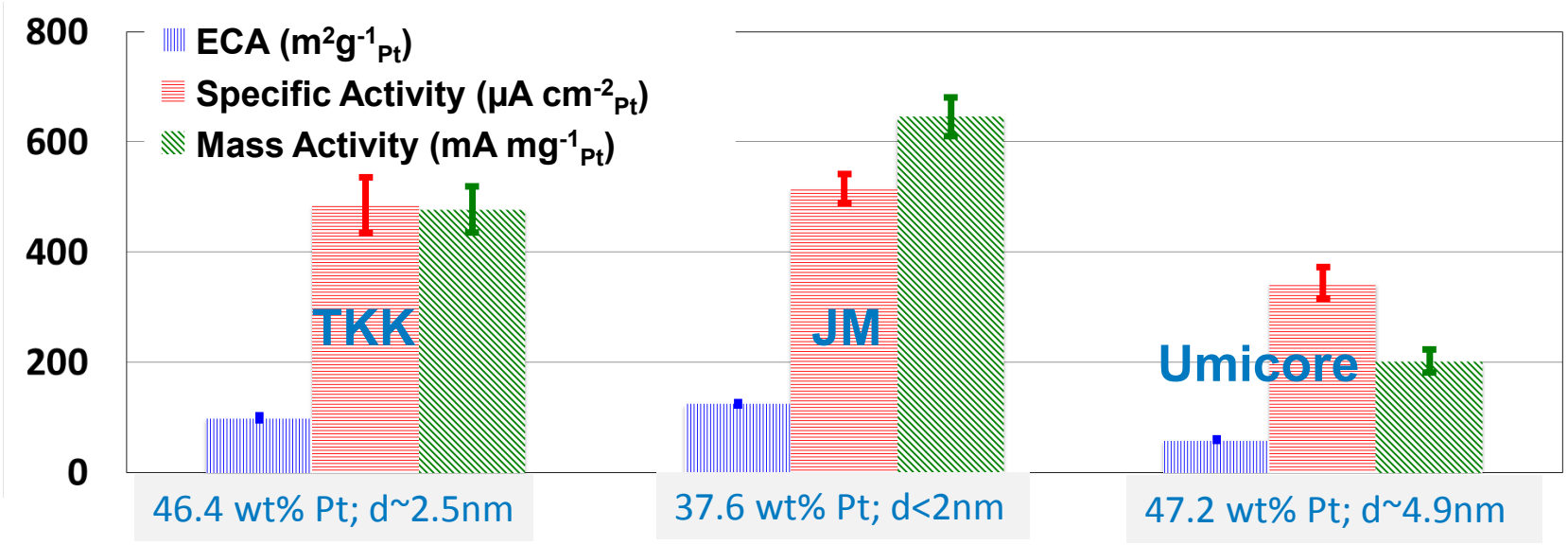


Measured specific activity is a function of: Impurities, electrode surface preparation and electrochemical conditioning.

Poly-Pt **specific activity (i_s) >2.0 mA/cm²$_{Pt}$** is an indicator of acceptable impurity levels in the cell/electrolyte.

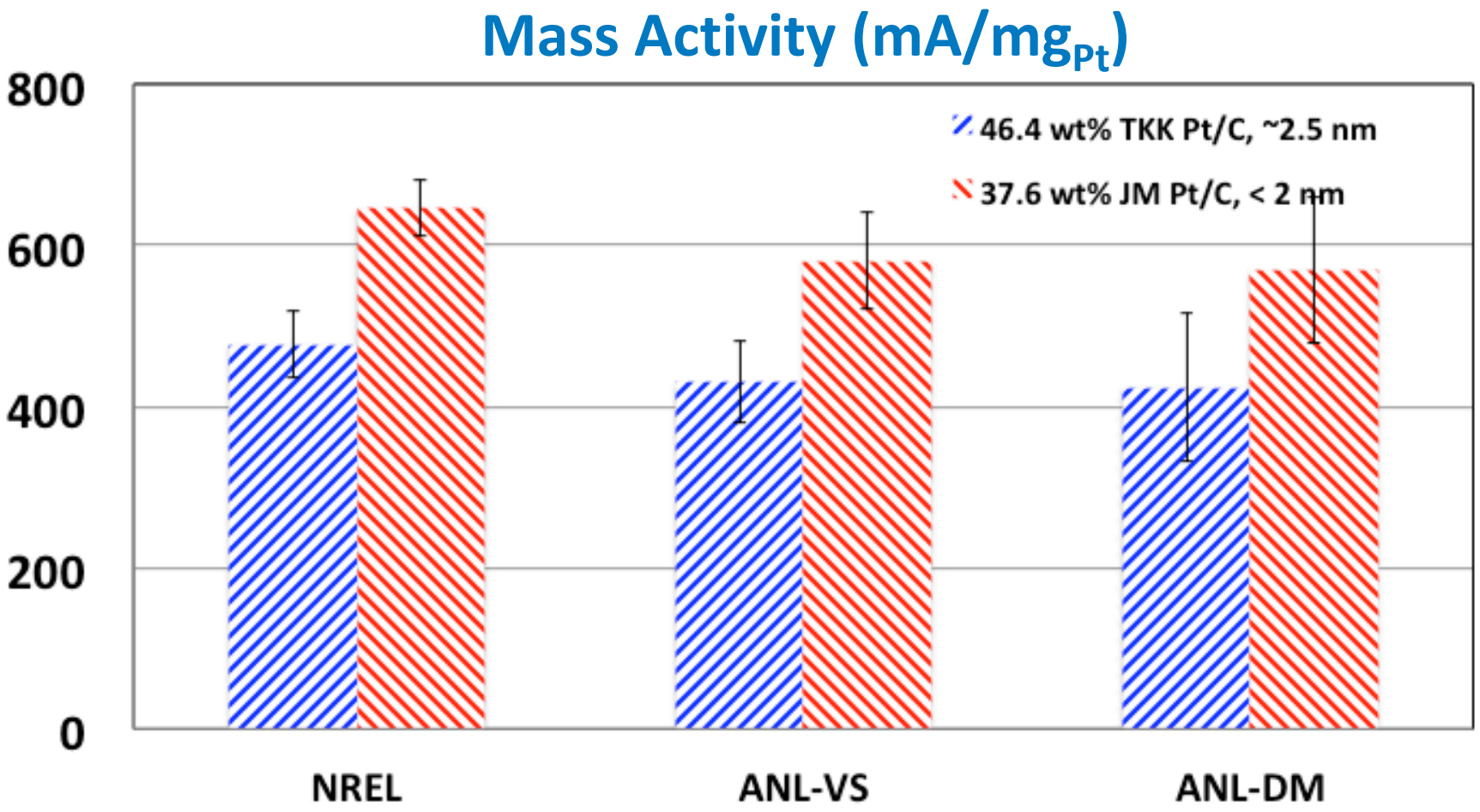
Catalyst Evaluation: Spin Coating





ECA, specific and mass activity for 3 Pt/C electrocatalysts @ NREL

Comparisons Between Labs



Pt/C catalyst mass activity measured between NREL and ANL labs.

Collaborations

Institutions	Role
National Renewable Energy Laboratory (NREL): Shyam Kocha (PI), Jason Zack, Kazuma Shinozaki, Svetlana Pylypenko	**Prime, oversees the project, selection of catalysts, investigation of protocols, ink dispersion, ink formulation and film deposition**
Argonne National Laboratory (ANL): Energy Conversion and Storage Group Vojislav Stamenkovic (co-PI), Yijin Kang, Joshua Snyder	**Participate as co-PI in selection of catalysts, protocols, & perform catalyst evaluation**
Argonne National Laboratory (ANL): Hydrogen and Fuel Cell Materials Group Deborah Myers (co-PI), Nancy Kariuki, Tammi Nowicki	**Participate as co-PI in selection of catalysts, protocols, & perform catalyst evaluation**
Tanaka Kikinzoku Kyogyo (TKK, Japan)	**Provide electrocatalysts, dry catalyst characterization**
Johnson Matthey (JM, UK)	**Provide electrocatalysts, dry catalyst characterization**
Umicore (Germany)	**Provide electrocatalysts, dry catalyst characterization**
University of the Western Cape & HySA (S. Africa): Bruno Pollet **Naval Research Laboratory (NRL):** Yannick Garsany	**Discuss/consult on RDE test methodology**

Interactions: Discussions with Catalysis Working Group & feedback from DOE RDE RFI responses

Proposed Future Work

- **Plans for the remainder of FY14**
  - Come up with and agree on a strategy on the logistics of distributing/shipping ~1g of electrocatalyst material (no charge) to those groups that are awarded a new electrocatalyst related project in upcoming DOE FOAs over the next ~5 years. [100 g of each catalyst available.]
  - Disseminate the results of the study (best practices for RDE and benchmark activity values) so that it is accessible to the PEM fuel cell electrocatalysis scientific community.

- **Plans for the next year (FY 15)**
  - We recommend a second phase of this study, where we evaluate easily available Pt-alloy/C catalysts, Pt/alternative carbon support catalysts to establish the status of these materials versus the baseline Pt/C materials. We also recommend an RDE durability study of these electrocatalyst materials.

Summary

- **Relevance:** Establish protocols and best practices for ink dispersion/film deposition/drying for rotating disk electrode (RDE) measurements to allow for more precise and reproducible data and reliable comparisons to be made between electrocatalyst development groups.
- **Approach:** To obtain electrocatalytic activity measurements:
  - for 2–3 commercially obtainable Pt/C electrocatalysts
  - for which the activity is measured a high degree of statistical reproducibility
  - using the same protocol and ink formulation and having the catalysts tested in 3 laboratories.
- **Accomplishments and Progress:**
  - Poly-Pt and 3 Pt/C nanoparticle electrocatalysts from major manufacturers were selected
  - A test protocol based on extensive study was selected
  - Cell cleaning, a variety of perchloric acid from different sources and the use of poly-Pt as cleanliness sensor was established
  - Of the various ink formulations/dispersion methods/coating and drying methods, the spin coating method was selected.
  - Poly-Pt, TKK and JM catalysts were evaluated to obtain activity and standard deviation values and are reported.
- **Collaborations:** 2 US national labs, 3 PEMFC industry catalyst vendors, Naval Research Labs and University of the Western Cape/HySA
- **Proposed Future Research:** Disseminate the results of the study (best practices for RDE and benchmark activity values) so that it is accessible to the PEM fuel cell electrocatalysis scientific community.

END

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Technical Back-Up Slides

TF-RDE References

H.A. Gasteiger et al., App. Catal. B: Environmental 56 (2005) 9.
Takahashi et al., J. Power Sources 195 (2010) 6312.
S. Kocha et al., ECS Trans., 50 (2) (2012) 1475.
K.J.J. Mayrhofer et al., Electrochim. Acta 53 (2008) 3181.
Y. Garsany et al., J. Electroanal. Chem. 662 (2011) 396.
E. Higuchi et al. J. Electroanal. Chem. 663 (2011) 84.
K. Ke et al., Electrochim. Acta 72 (2012) 120.

S. Kocha et al., ECS Trans., 50 (2) (2012) 1475.
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Y. Garsany et al., J. Electroanal. Chem. 662 (2011) 396.
Y. Garsany et al., J. Electrochem. Soc., 161 (5) (2014) F628.
M. Nesselberger et al., J. Am. Chem. Soc. 133 (2011) 17428.
W. Sheng et al., J. Electrochem. Soc., 159 (2) (2012) B96.
O.J. Curnick et al., RSC Advances, 2012, 2 (2012) 8368.

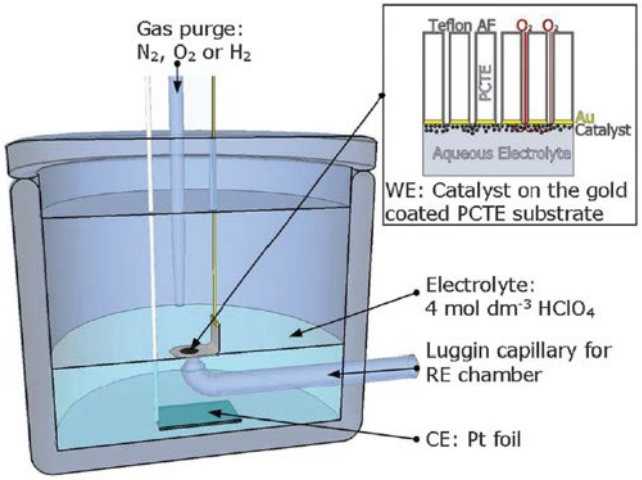
Electrocatalyst; Contaminants; Test Protocol; Corrections (iR, b.g.); Ink formulation, composition & dispersion; Film-uniformity; loading/thickness

R_{el}: electronic
R_{H+}: protonic
O_2 Diffusion
SO_3H Adsorption

True activity of Pt is unknown—what we have is a ‘measured activity’

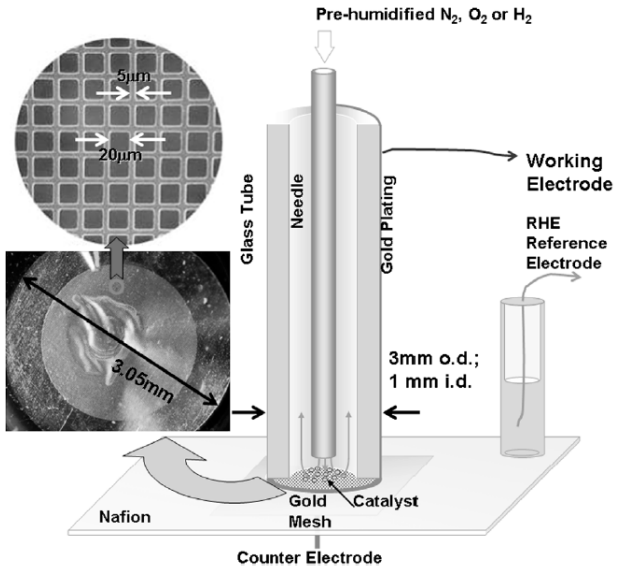
Other Half-Cell Techniques

Thin-film Floating Electrode



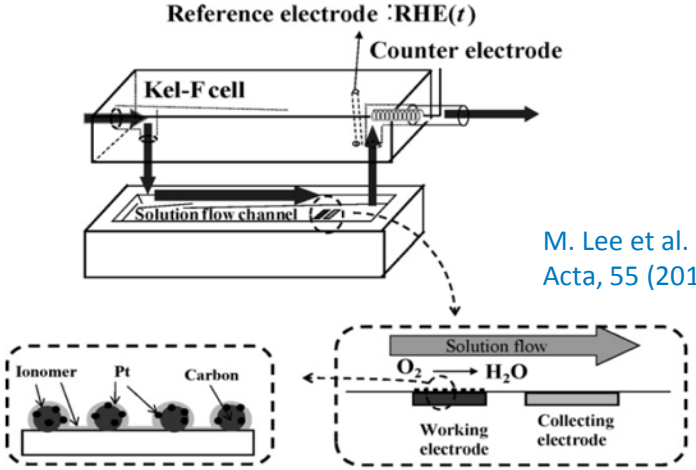
Zalitis, C. M.; Kramer, D.; Kucernak, A. R. *Phys. Chem. Chem. Phys.* **2013**, *15*, 4329

Wall-Jet



Kucernak, A. R.; Toyoda, E., *Electrochem. commun.* **2008**, *10*, 1728.

Channel Flow Dual Electrode



M. Lee et al. , Electrochim. Acta, 55 (2010) 8504–8512

Wakabayashi, N.; Takeichi, M.; Uchida, H.; Watanabe, M. *J. Phys. Chem. B* **2005**, *109*, 5836.

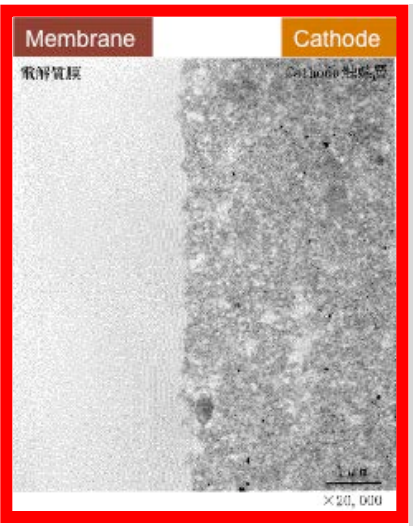
- Commercial availability
- Throughput
- Ease of cleaning cell
- Equipment Cost
- Value of measured activity
- Large i_{lim}/controlled i_{lim}
- Peroxide measurement

MEA vs. RDE: Materials, Structure, Mass-trans

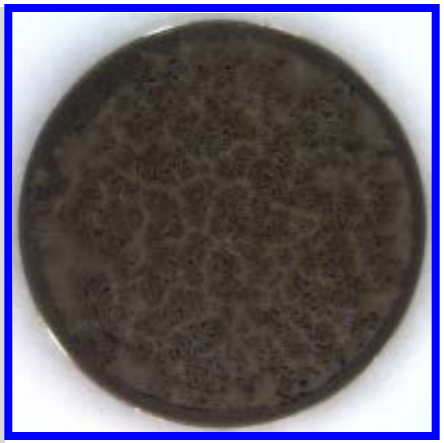
MEAs of PEMFCs

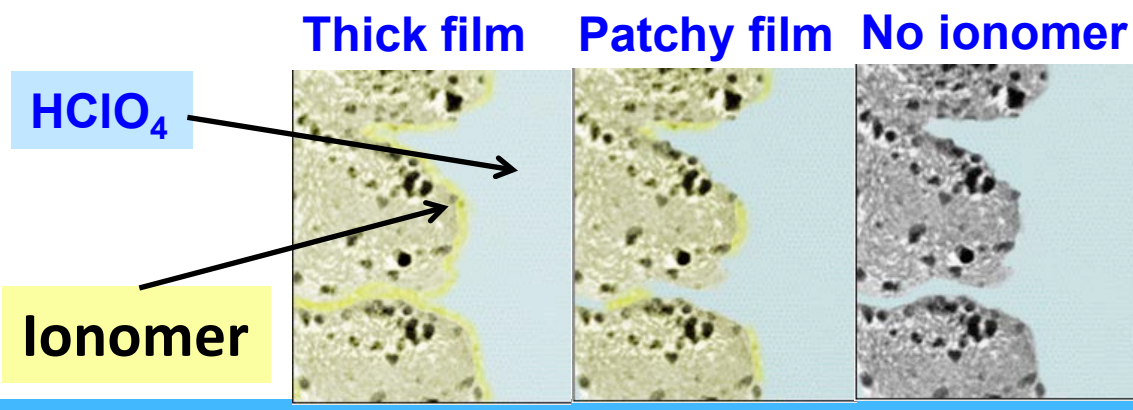
Electrocatalyst on Support

Thin-film RDE



- Oxygen Flow : Oxygen Saturated Acid
  Disk Rotation
- Pt/C | Nafion : Pt/C |Nafion | Acid
- Gas, H_2O, pores : Acid Flooded pores
- Electrode Thickness (~10 μm) : (0.3–4 μm)
- 100 % RH : Liquid Acid Electrolyte
- 15 min/point: Scan Rate:20 mV/s





Trends of catalyst activity and durability in RDE studies can be used to predict trends in PEMFCs