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Testing Oxygen Reduction Reaction Activity with the Rotating Disc Electrode Technique

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https://www1.eere.energy.gov/hydrogenandfuelcells/webinars.html

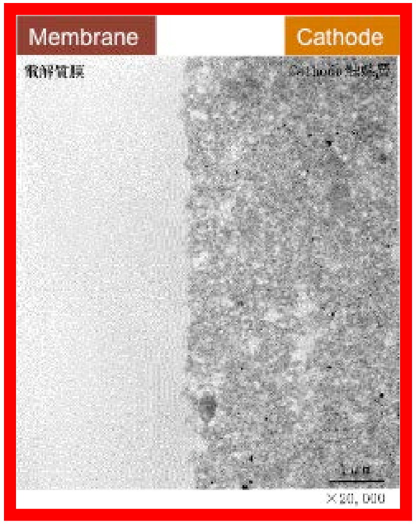
Outline

1) Background
2) Experimental Aspects of RDE Testing
3) Basic Measurement Technique & Analysis
4) Parameters Affecting RDE Activity Measurements
    1) Impact of Film Deposition & Drying Techniques
    2) Impact of Ink Formulation
    3) Impact of Nafion Incorporation
    4) Impact of particle size effects
    5) Correlation with MEA data
5) Electrocatalyst Durability using RDE Measurements
6) Summary

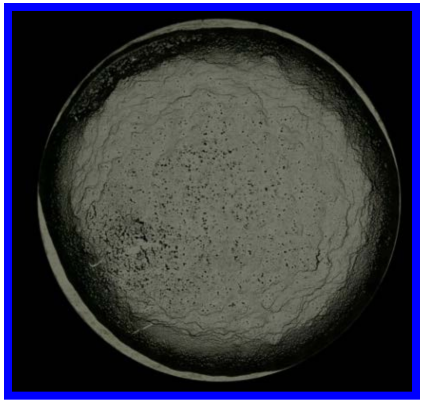
Background

PEMFC MEA

Thin-film RDE



O_2 Flow	Dissolved O_2
Pt/C | Nafion	Pt/C | Nafion | Acid
Gas & H_2O, pores	Acid Flooded pores
Electrode (5–15 μm)	Electrode (< 0.1 μm)
Nafion Ionomer	Perchloric Acid: H^+
Ionomer: H^+	Ionomer: Binder, Disp.
100 % RH	Liquid Electrolyte
15 min/point	Scan Rate: ~20 mV/s
100’s of mg Cat	10’s of mg Cat
$L = 0.2–0.4\ mg_{Pt}/cm^2$	$L = 4–36\ \mu g_{Pt}/cm^2$



5mm disk

Trends of activity and durability in Rotating Disc Electrode (RDE) studies can be used to predict **trends** in Proton Exchange Membrane Fuel Cells (PEMFCs).

Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

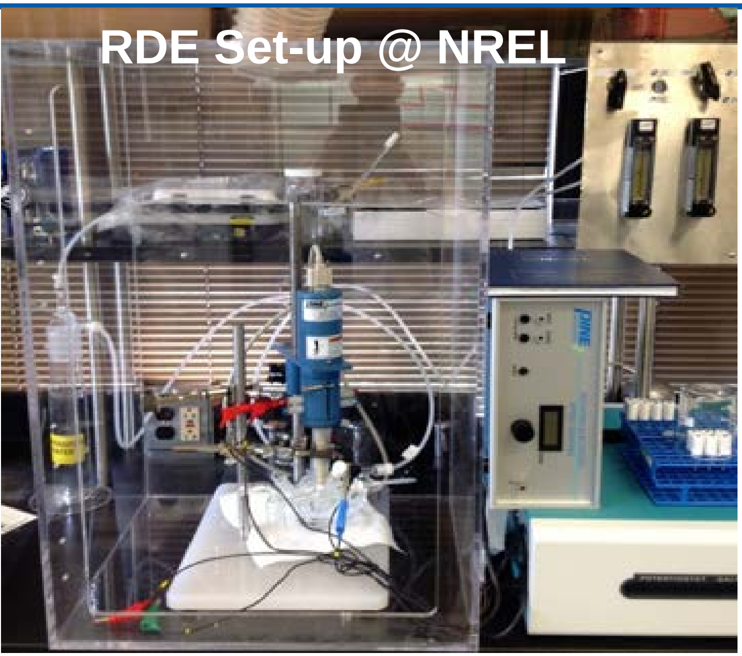
Information Obtainable from RDE Measurements

Besides its usefulness as a tool to predict electrocatalyst activity and durability in fuel cells, the RDE technique allows us to carry out the following diagnostics.

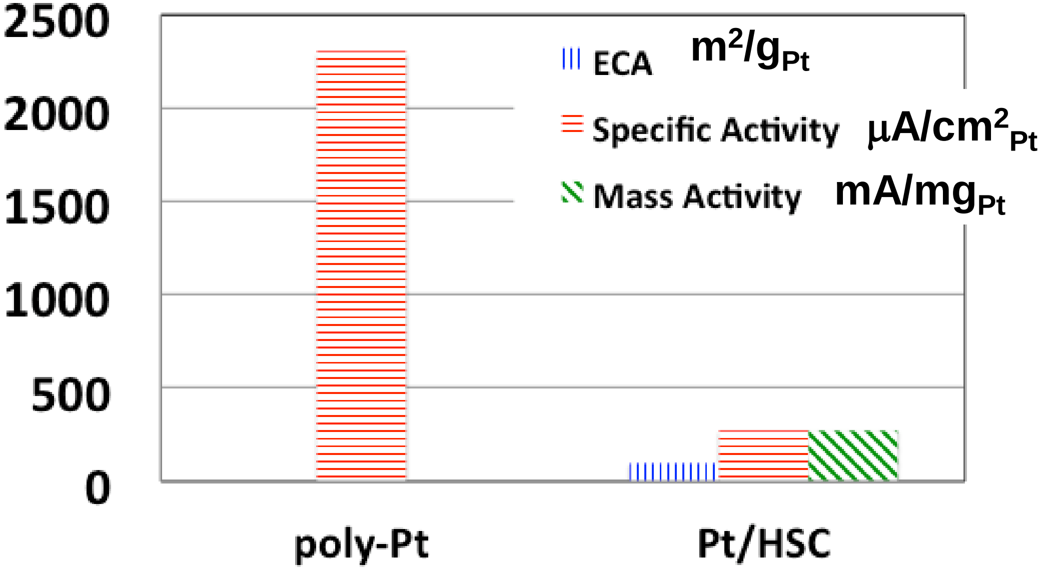
- **Cyclic Voltammograms under N_2**
  - HUPD ➔ ECA (m^2/g)
  - CO Chemisorption➔ ECA (m^2/g)
  - Cu UPD➔ ECA (m^2/g)
  - Double Layer Capacitance
  - Pseudo-Capacitance (oxide coverage)
  - Onset potential of support corrosion
  - Short term durability for thousands of cycles
- **I–V Curves under O_2**
  - Electrocatalyst specific and mass Activity
    - Poly-Pt, Pt/C, Pt-alloy/C, Pt core-shell/C, Extended thin films, NPGM
  - Reaction Order w.r.t. PO_2
  - Tafel slopes
  - Effect of contaminants in electrolyte or reactant gases
  - Electrolyte anion adsorption
- **Peroxide Generation using Ring disc (RRDE)**
- **Complementary Techniques**
  - EIS, EQCN, etc.,

Experimental Aspects of RDE Testing

Electrochemical Set-up/Glassware Cleaning



Activity & ECA @ 0.90 V, 100 kPa, 25°C



Concentrated Acid/Oxidant

Boiling in DI Water

Using poly-Pt disk & obtaining specific activity values of $I_s > 2.0\ mA/cm^2_{Pt}$ can be considered a measure of acceptable cell cleanliness.

Contamination of cell/electrolyte poisons the catalyst and is one of the primary reasons for low and scattered activity data.

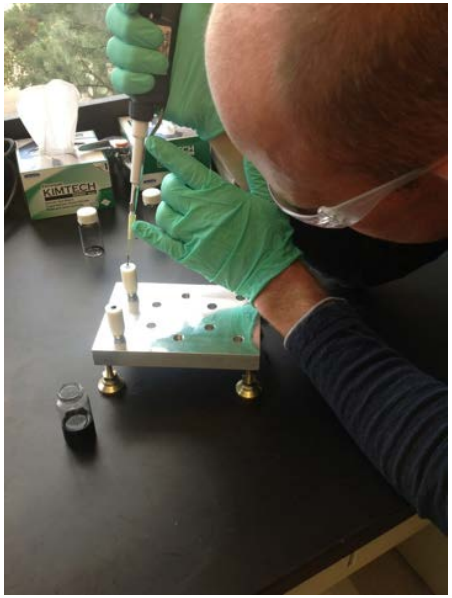
Ink Formulation, Electrode Preparation

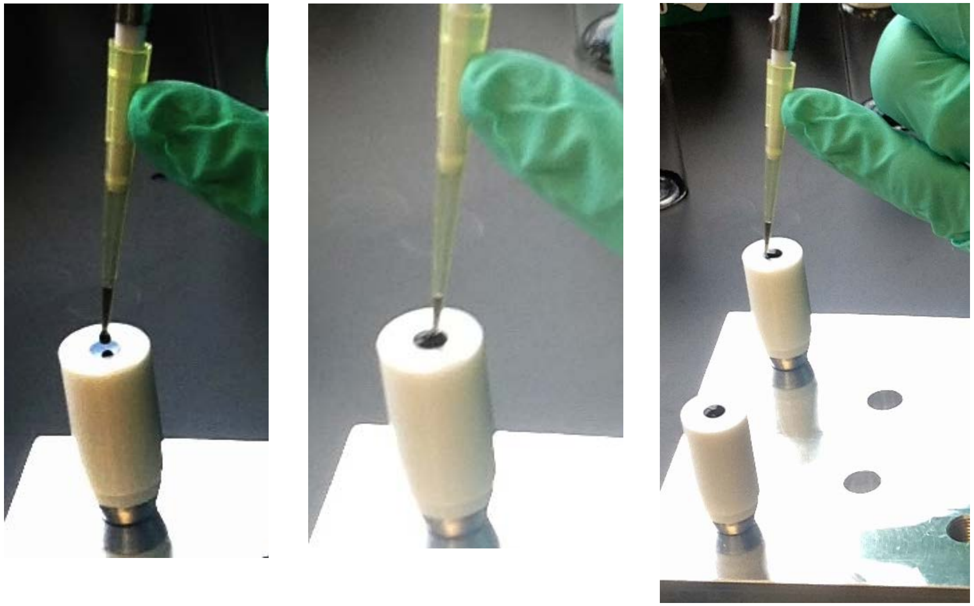
Bath Sonicator

Nanobalance

Horn Sonicator

Ink Deposition

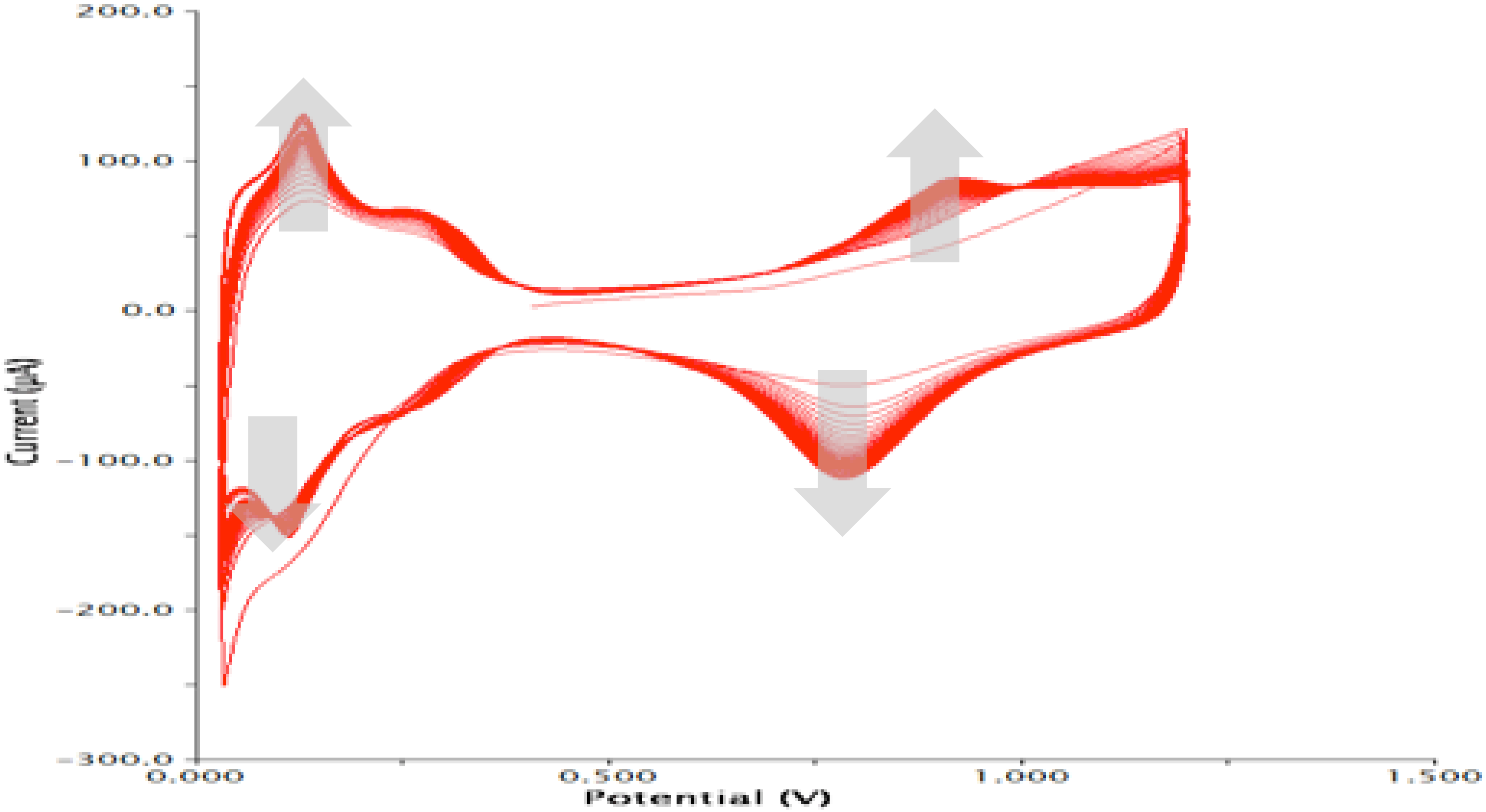




Kocha, S. S., et al., ECS Trans. 2012, **50**.

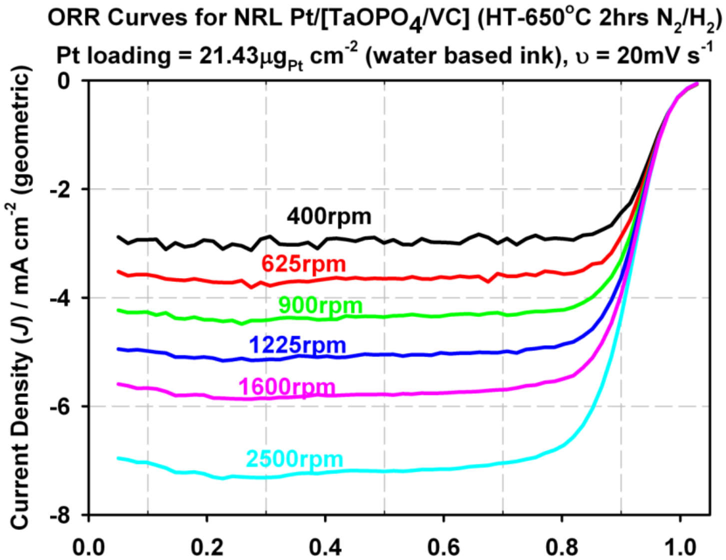
RDE Conditioning or Break-in

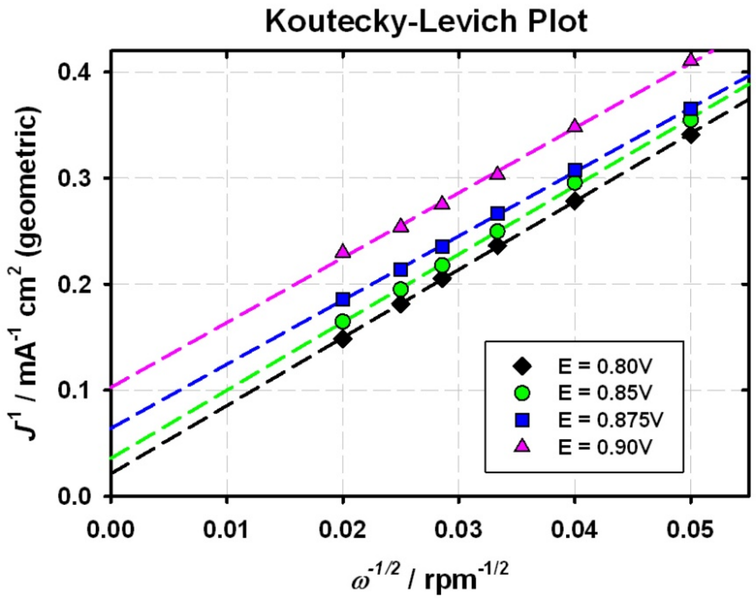
0.05–1.2 V, 100 mV/s, ~50 cycles, Pt/C, 25^{o}C, N_2

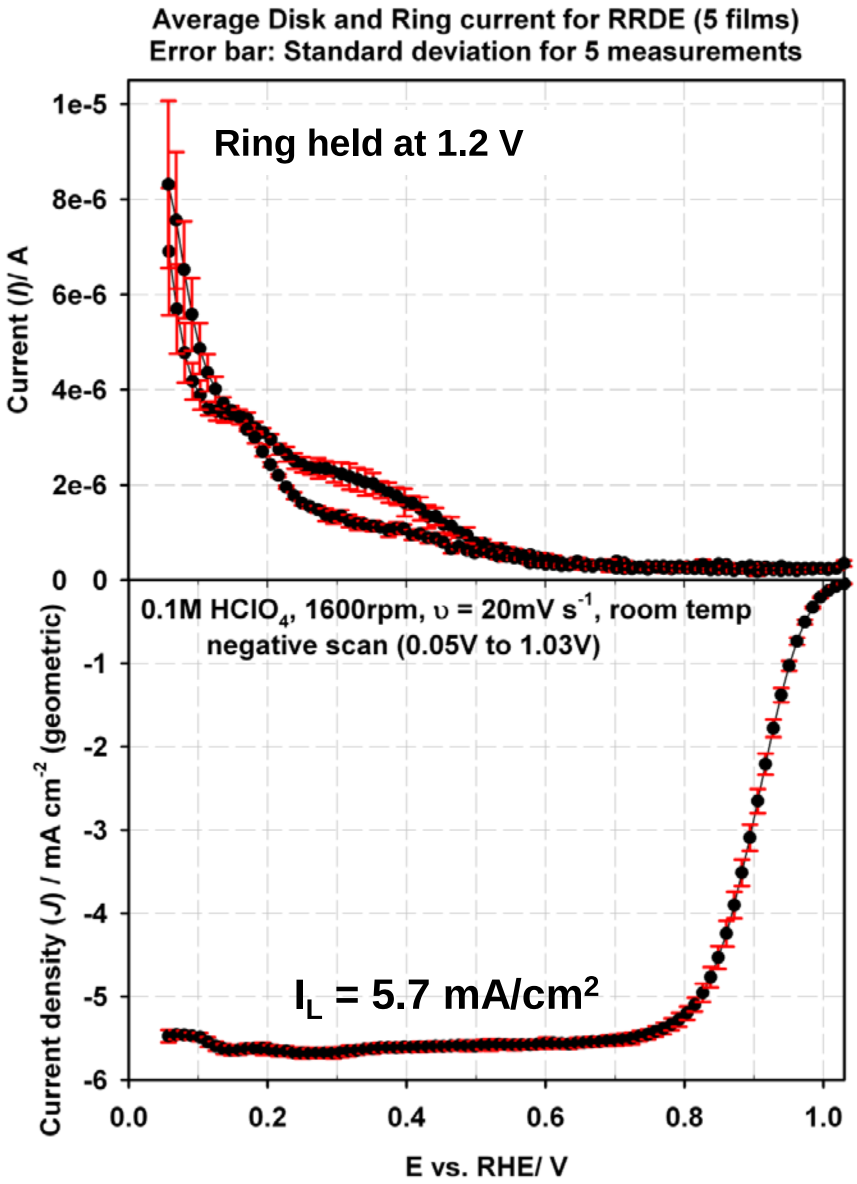


Conditioning protocol may have to be varied with electrocatalyst material. Conditioning is complete <u>when the CV becomes invariant</u> with time, cycles.

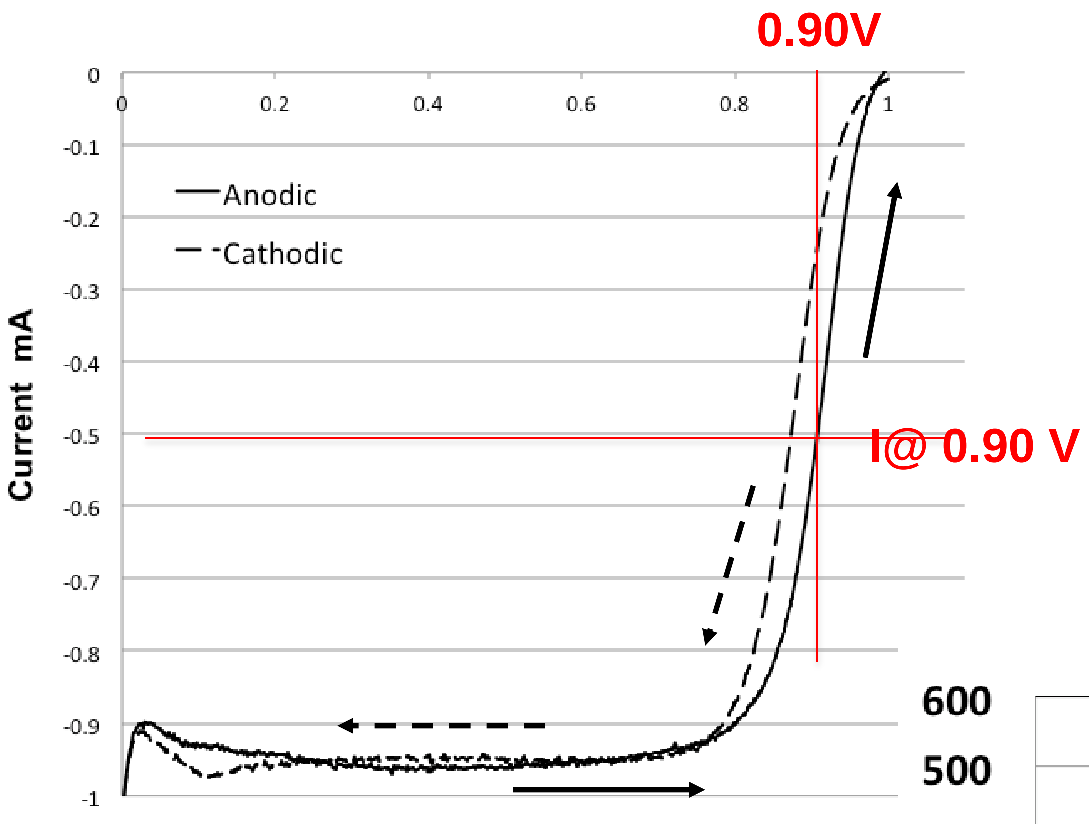
RDE Analysis



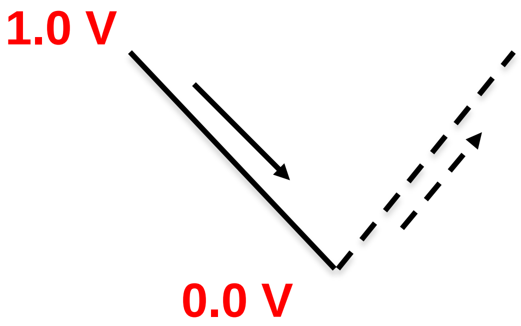




RDE Test Protocol

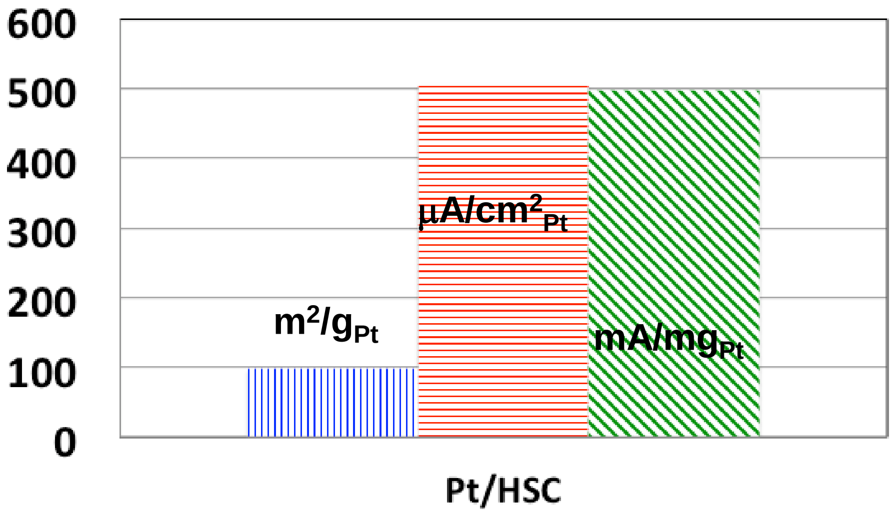


Voltage Profile Protocol



Protocol parameters such as: Scan Direction, Scan Rate, and Voltage Range will affect the measured catalyst activity.

0.90 V, 20 mV/s, 0–1.0 V, 1600 rpm, cathodic scan, 25°C, 0.1M $HClO_4$, iR corrected, background current corrrected & corrected to 100 kPa reaction order w.r.t O_2 of 0.85.



Corrections Applied to ORR I-V Curves

➢Background current correction

At lower potential scan rates, the effect of impurities and the formation of surface oxides suppress the measured ORR activity; at scan rates above 20mV s^{-1}, capacitive current effects are higher. The background current is measured by running the ORR sweep profile (e.g., 1.03 V→0.05 V→1.03 V at 5 and 20 mV s^{-1} and 1600 rpm) in N_2–purged 0.1 M $HClO_4$ either before or after the ORR measurements to account for capacitive current contributions. This background current is subtracted from the experimental ORR current to eliminate any contributions of capacitive current.

➢Measurement and active compensation of solution resistance

Solution resistance is caused by a combination of low electrolyte concentration and temperature as well as the distance of the Luggin capillary or Reference electrode to the surface of the working electrode. Expected value for resistance in 0.1 M perchloric acid is ~20 ohms.

V. Stamenkovic et al., "On the importance of correcting for the uncompensated ohmic resistance in model experiments of the Oxygen Reduction Reaction", J. Electroanal. Chem. 647 (2010) 29-34.

➢Corrections for oxygen partial pressure

The atmospheric pressure decreases with altitude and so labs such as those at NREL, Golden, CO (~6000 ft, ~83 kPa) have to apply a correction for limiting current as well as kinetics so that the data is normalized to 100 kPa O_2. Limiting currents are expected to be ~5.7 mA/cm^2 @ 1600 rpm when corrected to 100 kPa O_2.

Parameters Affecting RDE Measurements of Electrochemical Activity

Parameters Affecting RDE Measurements

Ink Formulation

- Type of Solvent
- Water/Solvent/Nafion
- Ultrasonication type, time and intensity

Electrode

- Surface Preparation: Polishing, cleaning
- Material: GC, Au, etc
- **Film Quality and uniformity**

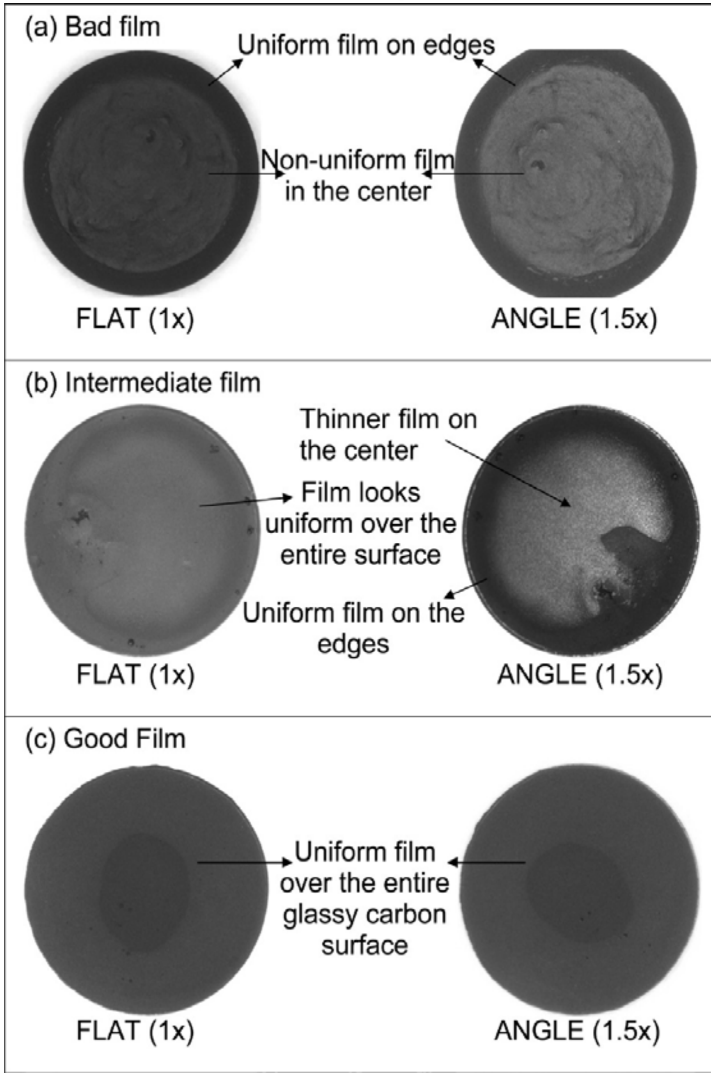
Deposition & Drying of Film on Electrode

- **Rotating/Stationary**
- Atmosphere: N_2, air, other
- Gas Flow Rate
- Temperature

A number of factors affect the "<u>measured activity</u>" of catalysts in RDE measurements besides the obvious measurement protocol, operating test conditions & proper analysis/corrections applied to the data.

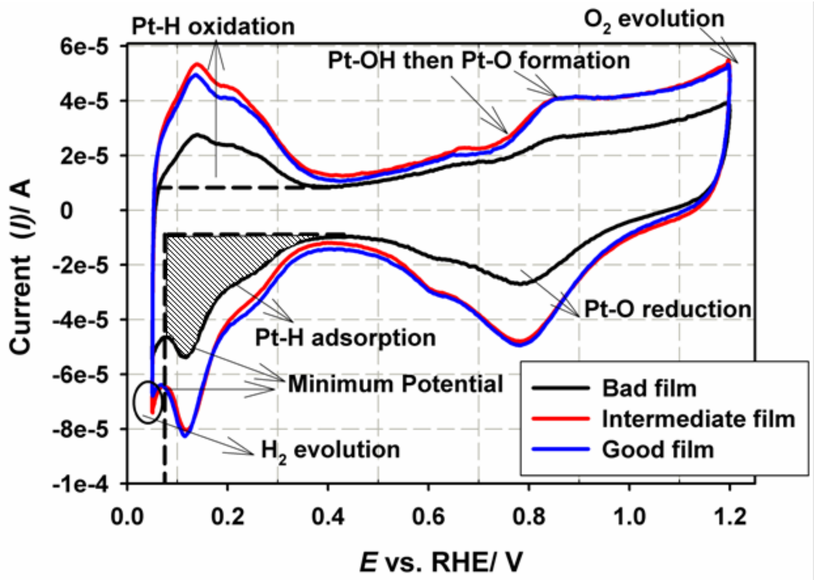
Stationary Drying: Film Quality

19.7% Pt/VC (ETEK)

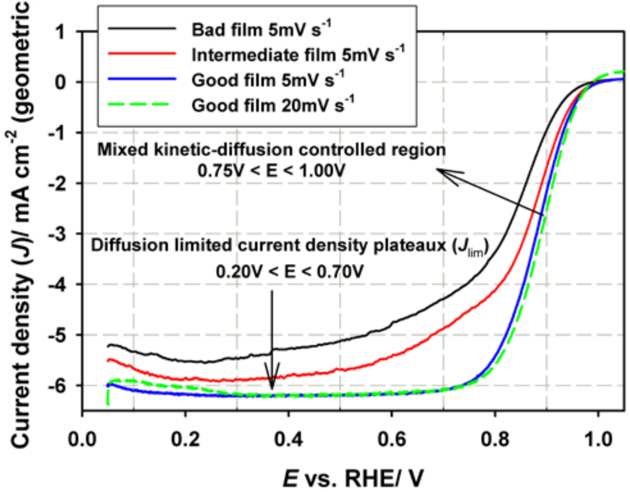


Y. Garsany, O.A. Baturina, K.E. Swider-Lyons, S.S. Kocha, Experimental Methods for Quantifying the Activity of Platinum Electrocatalysts for the Oxygen Reduction Reaction, Anal. Chem. 82 (2010) 6321-8.

Typical cyclic voltammogram (CV) recorded for Pt/C catalyst in N_2-purged 0.1M $HClO_4$



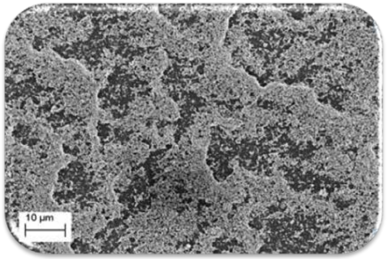
Typical ORR curves recorded for Pt/VC catalyst in O_2-purged 0.1M $HClO_4$



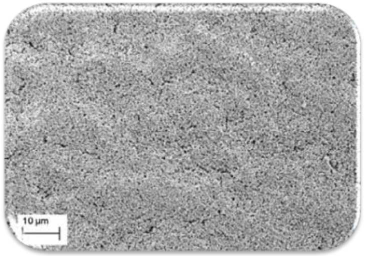
Stationary drying: Thin-film Morphology

a) optical microscope

- ➢Fairly uniform on the edge of electrode
- ➢Thinner region towards the center of electrode
- ➢Coffee ring structure at the edge

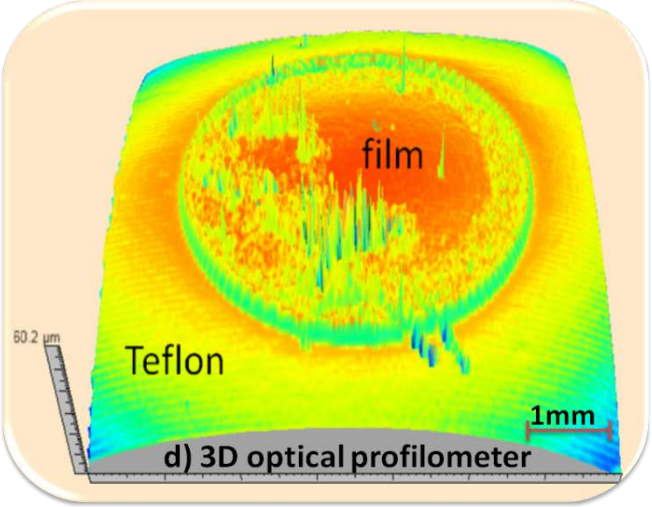


b) SEM center of electrode



c) SEM edge of electrode

- ➢Center: Non-homogeneous, not fully covered
- ➢Edge: Fairly dense and homogenous



d) 3D optical profilometer

- ➢Non uniform film thickness
- ➢Coffee ring structure apparent near the edge
- ➢Regions of great non-homogeneity throughout the film

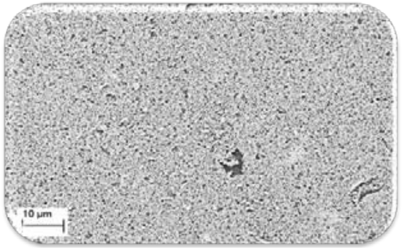
Y. Garsany, I.L. Singer, and K.E. Swider-Lyons, Impact of film drying procedures on the RDE characterization of Pt/VC electrocatalyst, J. Electroanal. Chem. 662 (2011) 396-406.

PJ Yunker *et al. Nature* **476**, 308-311 (2011) doi:10.1038/nature10344

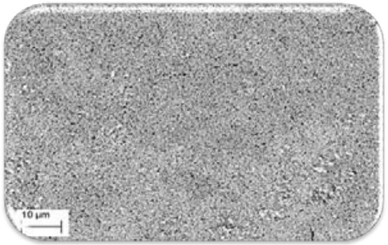
Rotational drying: Thin-film Morphology

a) optical microscope

- ➢Very uniform over the entire GC surface
- ➢No Coffee ring structure visible

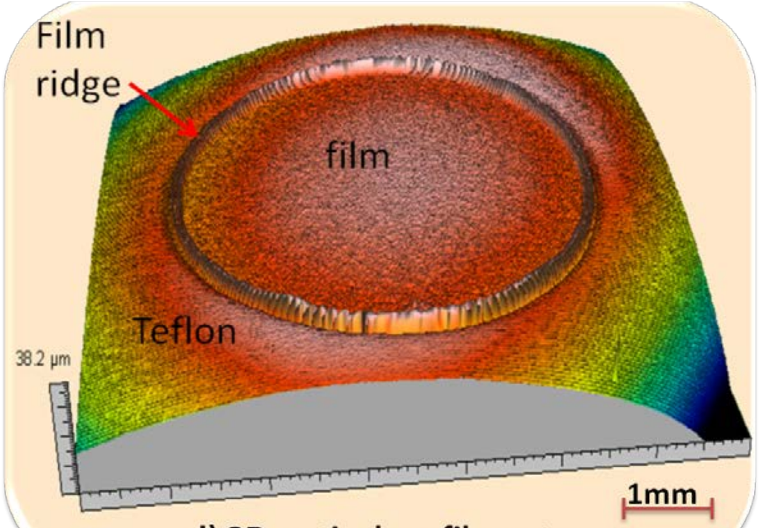


b) SEM center of electrode



c) SEM edge of electrode

- ➢ Dense film covering the entire GC surface

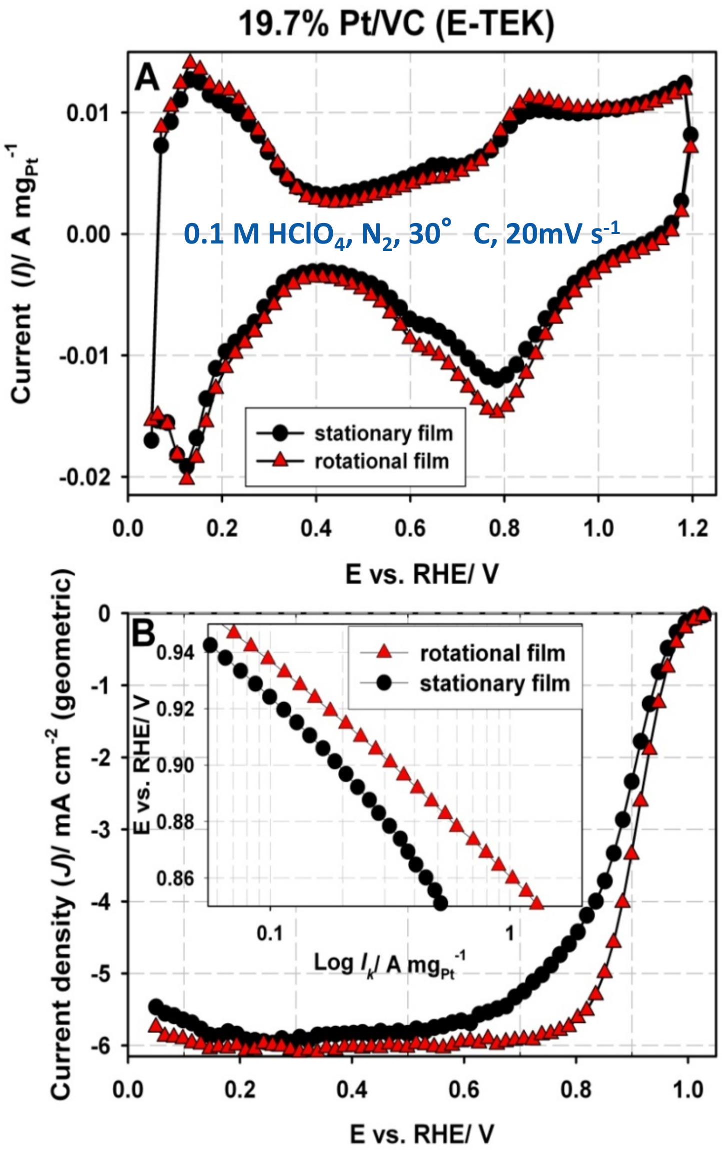


d) 3D optical profilometer

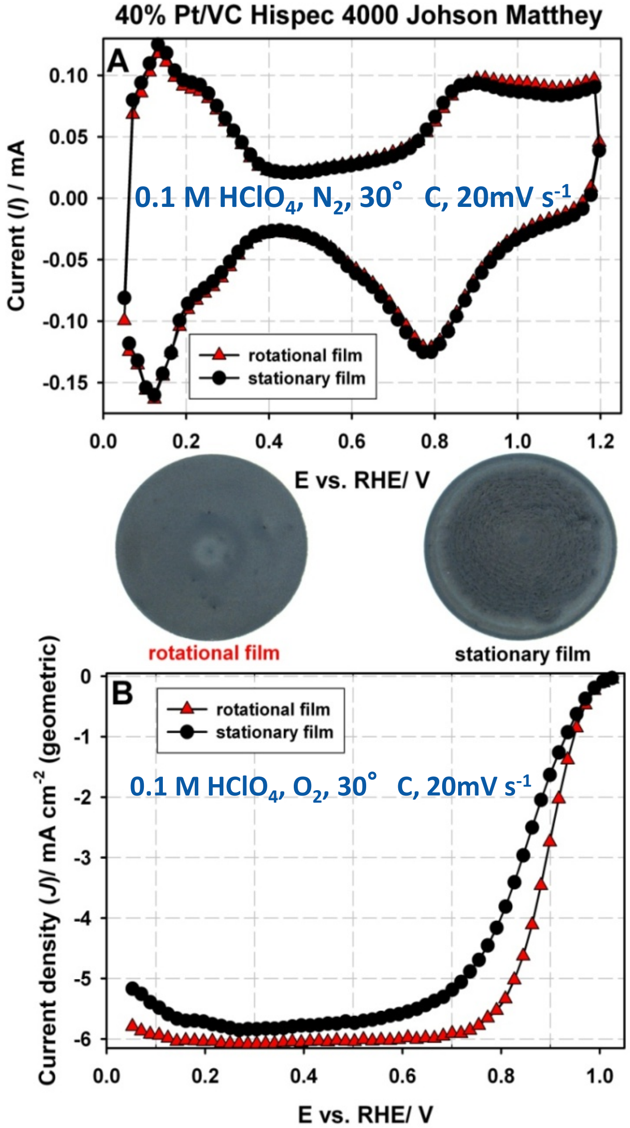
- ➢The 3D picture obtained for the rotational film clearly demonstrates that the rotational drying method produced a uniform film over the entire glassy carbon surface

Y. Garsany, I.L. Singer, K.E. Swider-Lyons, J. Electroanal. Chem. 662 (2011) 396-406.

Drying method: Electrochemical Performance



0.1 M $HClO_4$, N_2, 30° C, 20mV s^{-1}

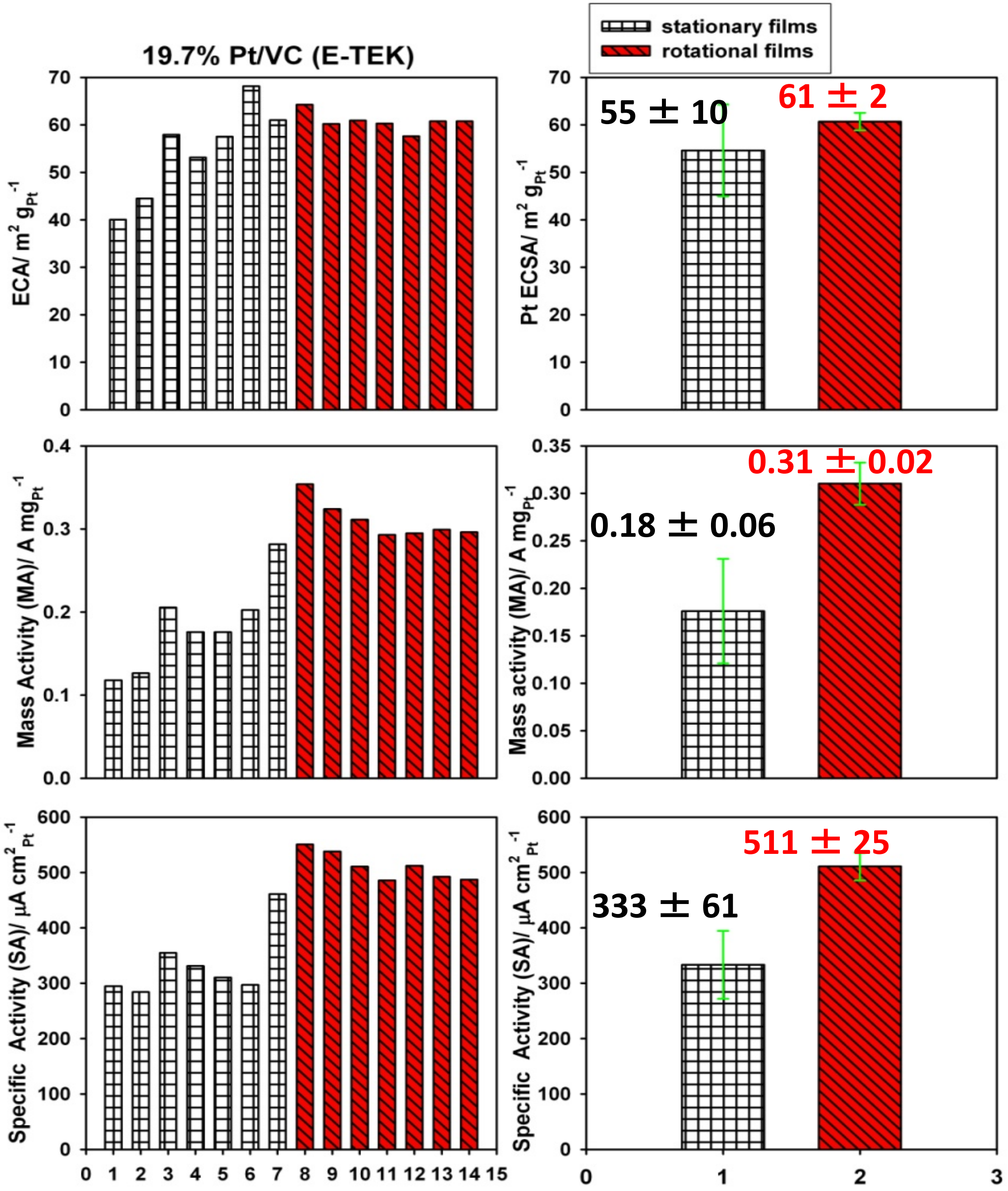


0.1 M $HClO_4$, N_2, 30° C, 20mV s^{-1}

0.1 M $HClO_4$, O_2, 30° C, 20mV s^{-1}

Y. Garsany, I.L. Singer, and K.E. Swider-Lyons, J. Electroanal. Chem. 662 (2011) 396-406.

Reproducibility: Rotational vs. Stationary Drying



Y. Garsany, I.L. Singer, and K.E. Swider-Lyons, J. Electroanal. Chem. 662 (2011) 396-406.

Parameters Affecting RDE Measurements

Ink Formulation

- Type of Solvent
- **Water/Solvent/Nafion**
- Ultrasonication type, time and intensity

Electrode

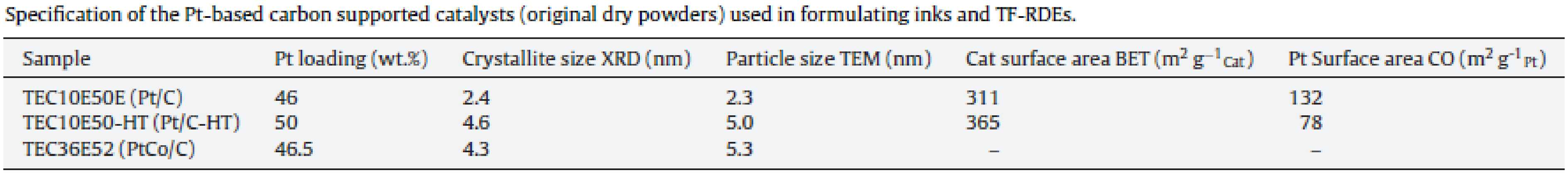
- Surface Preparation: Polishing, cleaning
- Material: GC, Au, etc

Deposition & Drying of Film on Electrode

- Atmosphere: N_2, air, other
- Gas Flow
- Temperature

A lot of time and effort is spent on optimizing the ink formulation for catalyst layers in MEAs of PEMFCs. Is such an optimization necessary for RDE films?

Activity: Water/IPA Ratio Optimization for Catalysts



Specification of the Pt-based carbon supported catalysts (original dry powders) used in formulating inks and TF-RDEs.

Sample	Pt loading (wt.%)	Crystallite size XRD (nm)	Particle size TEM (nm)	Cat surface area BET ($m^2\,g^{-1}{}_{Cat}$)	Pt Surface area CO ($m^2\,g^{-1}{}_{Pt}$)
TEC10E50E (Pt/C)	46	2.4	2.3	311	132
TEC10E50-HT (Pt/C-HT)	50	4.6	5.0	365	78
TEC36E52 (PtCo/C)	46.5	4.3	5.3	–	–

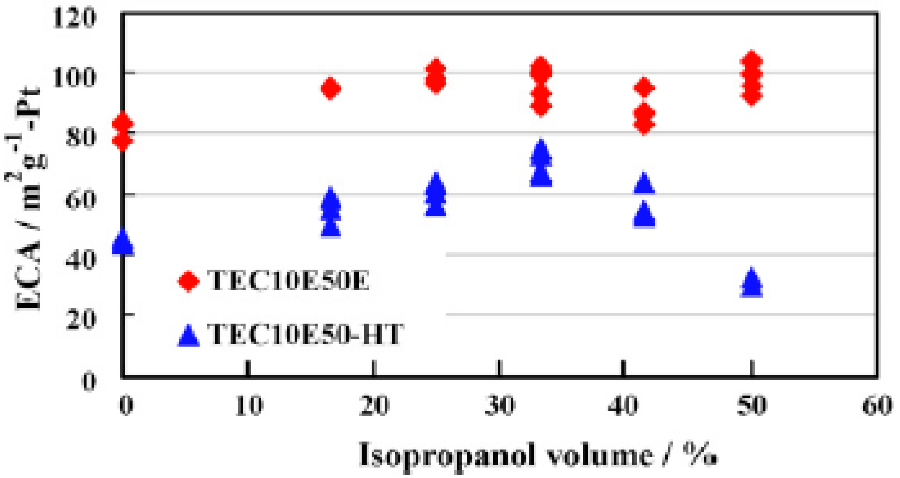


Fig. 2. ECA ($m^2\,g^{-1}$) values plotted as a function of isopropanol content for different ink compositions (Pt/C + water + isopropanol). The inks were used to prepare TF-RDEs and ECA measured in 0.5 M H_2SO_4. The ECA shows a pronounced peak in magnitude for about 35% IPA composition for the Pt/C-HT and Pt-alloy/C whereas the peak is rather shallow for the Pt/C baseline catalyst. All inks had identical ultrasonication times of 30 min.

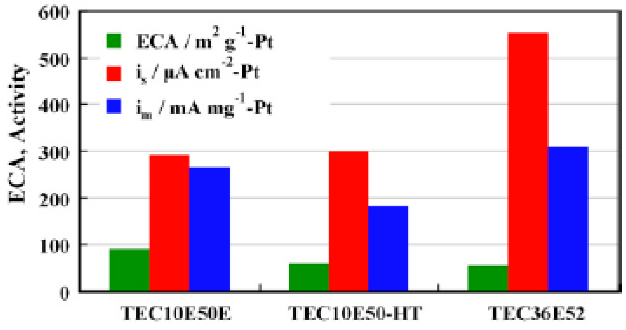
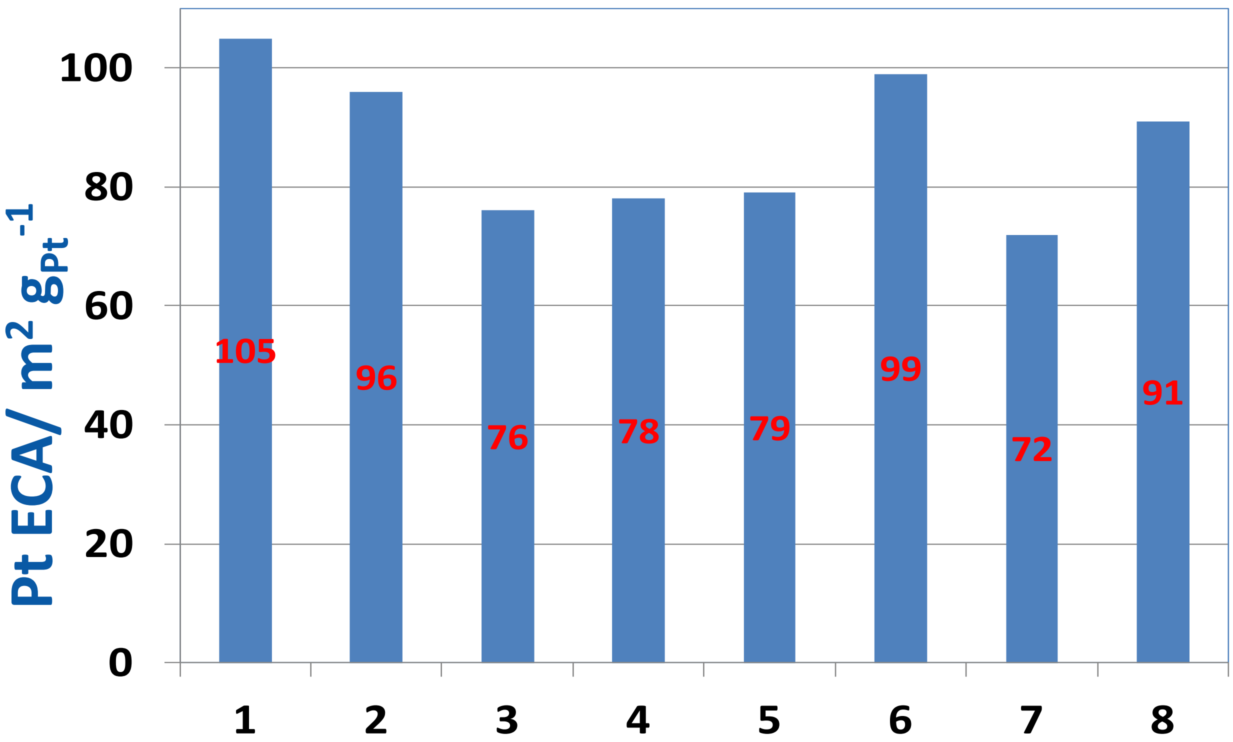


Fig. 6. ECA, specific activity i_s and mass activity i_m for 3 Pt-based catalysts (Pt/C, Pt-HT/C and PtCo/C) measured using optimum ink formulations in 0.1 M perchloric acid at 25 °C. The PtCo/C shows a lower ECA, a significantly higher specific activity (1.8×) compared to the baseline Pt/C and a slight enhancement of mass activity.

Takahashi, Ikuma, and Shyam S. Kocha. "Examination of the activity and durability of PEMFC catalysts in liquid electrolytes." ***Journal of Power Sources*** **195, no. 19 (2010): 6312-6322.**

ECA: Impact of Ink Formulation

Pt ECA varies from 72m^2 g$_{Pt}$$^{-1}$ to 105m^2 g$_{Pt}$$^{-1}$



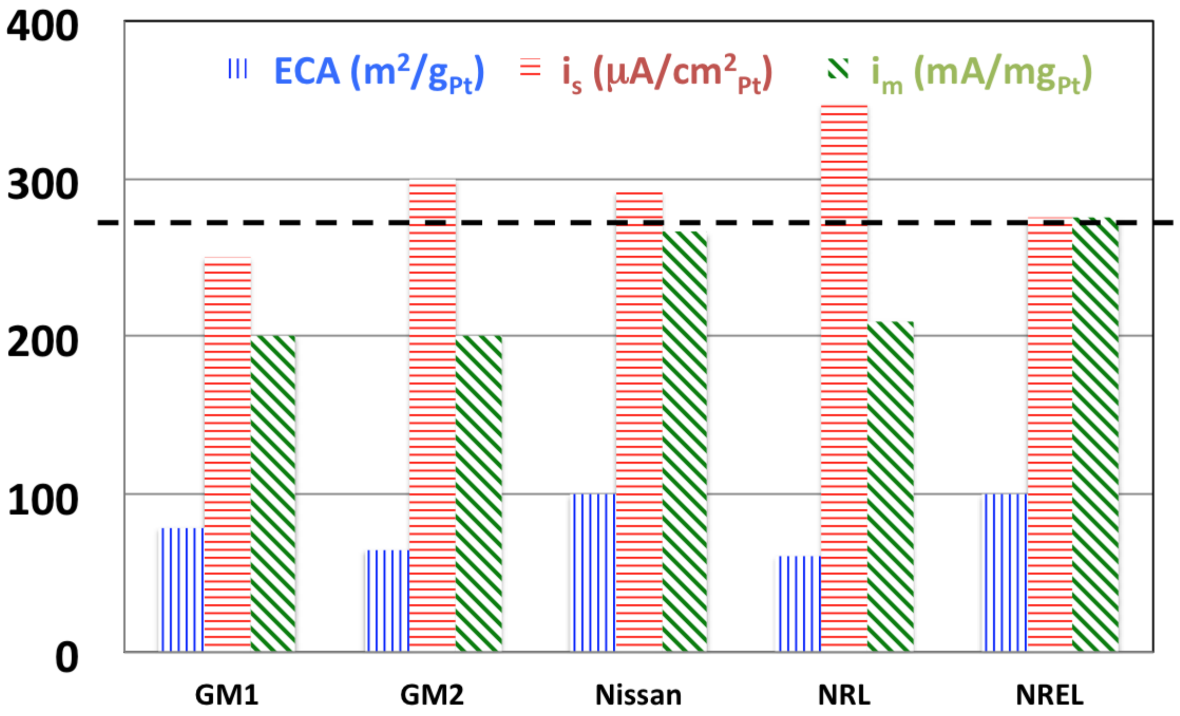
TKK Pt/C (HSC) catalyst
TEC-10E50E (50% Pt/C)

INK FORMULATION

1: Water/IPA/Nafion (optimized)
2: Water/Nafion film
3: Water/Nafion film
4: Water/Nafion film
5: Water/Ethanol/Nafion
6: Water/IPA/Nafion
7: IPA/Nafion
8: Water/IPA/Nafion

1: Kocha et al., J. Power Sources 195 6312-6322 (2010).
2: Y. Shao-Horn et al., Electrochem Solid St, 14 (10) B110-B113 (2011).
3: Arenz et al., J. Am. Chem. Soc., 133, 17428-17433, (2011).
4: Y. Shao-Horn et al., J. Electrochem. Soc, 159 (2) B96-B103 (2012).
5: Morimoto et al., Electrochimica Acta, 72, 120-128, (2012).
6: Kocha et al., ECS Transaction 50 (2) 1475-1485 (2012).
7: Garzon et al., ECS Transaction 50 (2) 1693-1699 (2012).
8: Pollet et al., RSC Advances, 2, 8368-8374, (2012).

Baseline Pt/C Activity Benchmarks in RDE



(GM1) TKK 46 wt% Pt/HSC, 60°C, 20 mV/s, no iR comp

(GM2) E-TEK 20 wt% Pt/V, 60°C, 20 mV/s, no iR comp

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

(NRL) E-TEK 20 wt% Pt/V, 25°C, 20 mV/s, no iR comp

(NREL) TKK 46 wt% Pt/HSC, 25°C, 20 mV/s, iR comp

H. A. Gasteiger, S. S. Kocha, et al. , *Appl. Catal. B-Environmental*, **56**, 9 (2005).

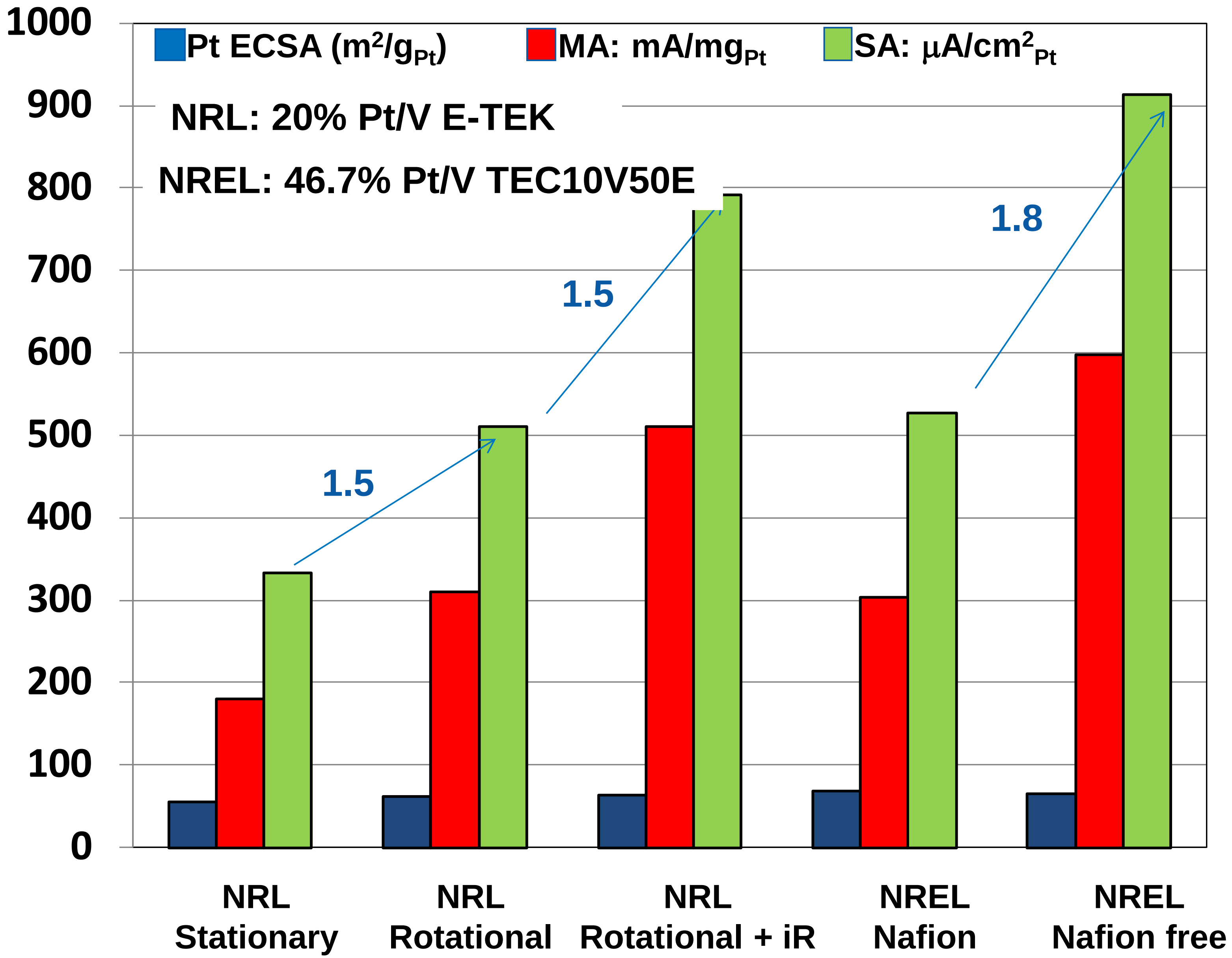
I. Takahashi et al., *J. Power Sources*, **195**, 6312 (2010).

Y. Garsany, et al., *Anal. Chem.*, **82**, 6321 (2012).

Ionomer/Carbon Ratio ~ 0.5

All above electrodes were formulated incorporating Nafion in inks. Comparable results can be obtained at different labs for similar quality films.

Activity: Impact of Ink Formulation



Parameters Affecting RDE Measurements

Nafion ionomer in the film can cause:
—Oxygen transport resistance
—Electronic resistance
—Anion adsorption
—Help disperse the catalyst
—Act as a binder for the catalyst film

Ink Formulation

- Type of Solvent
- Water/Solvent/**Nafion**
- Ultrasonication type, time and intensity

Electrode

- Surface Preparation: Polishing, cleaning
- Material: GC, Au, etc
- Film Quality and uniformity

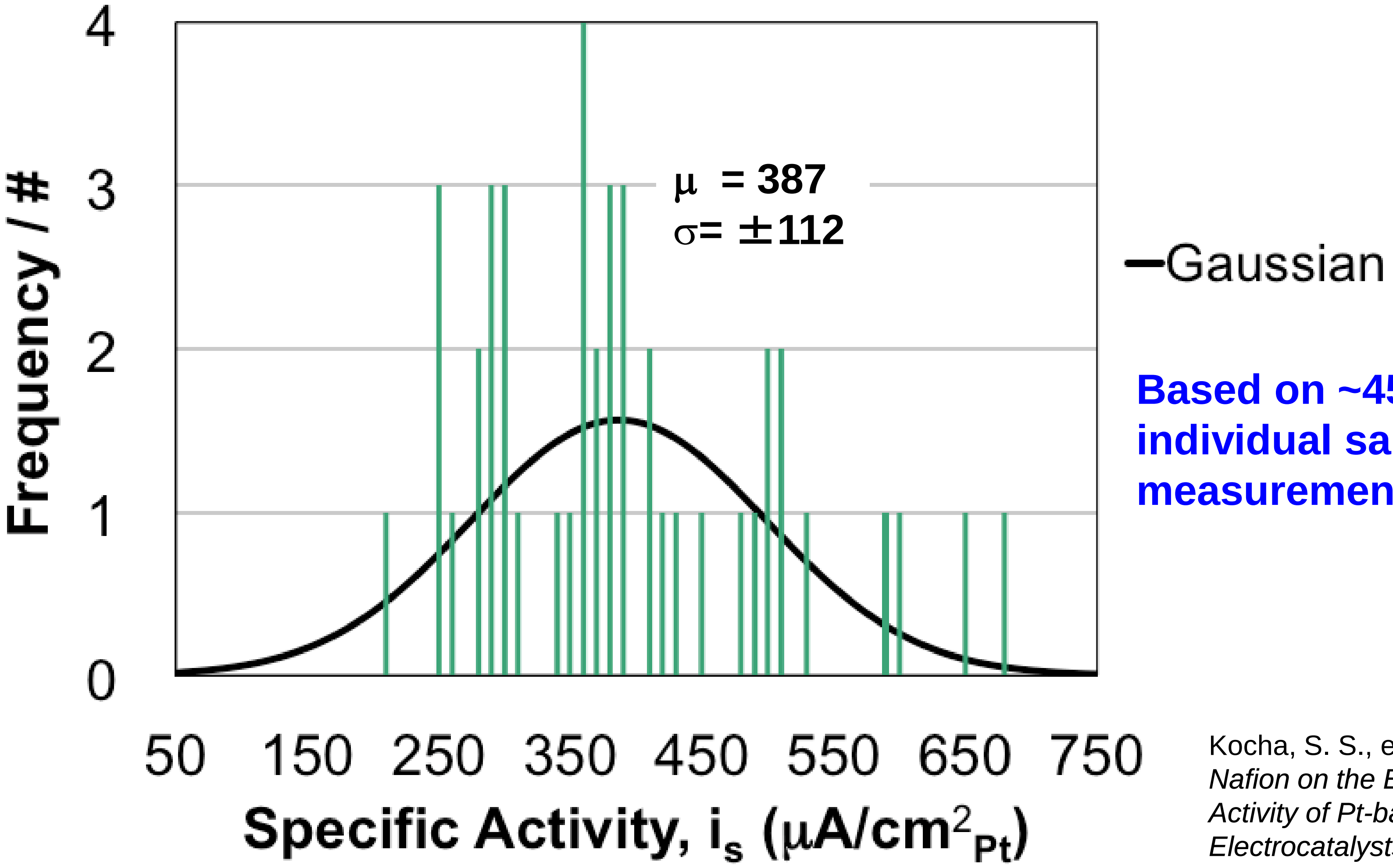
Deposition & Drying of Film on Electrode

- Rotating/Stationary
- Atmosphere: N_2, air, other
- Gas Flow Rate
- Temperature

Nafion function is primarily a binder in RDE electrodes and is not essential for H^+ conduction since the acid electrolyte provides protons.

can it be eliminated?

Nafion-free Ink Formulation— Pt/HSC

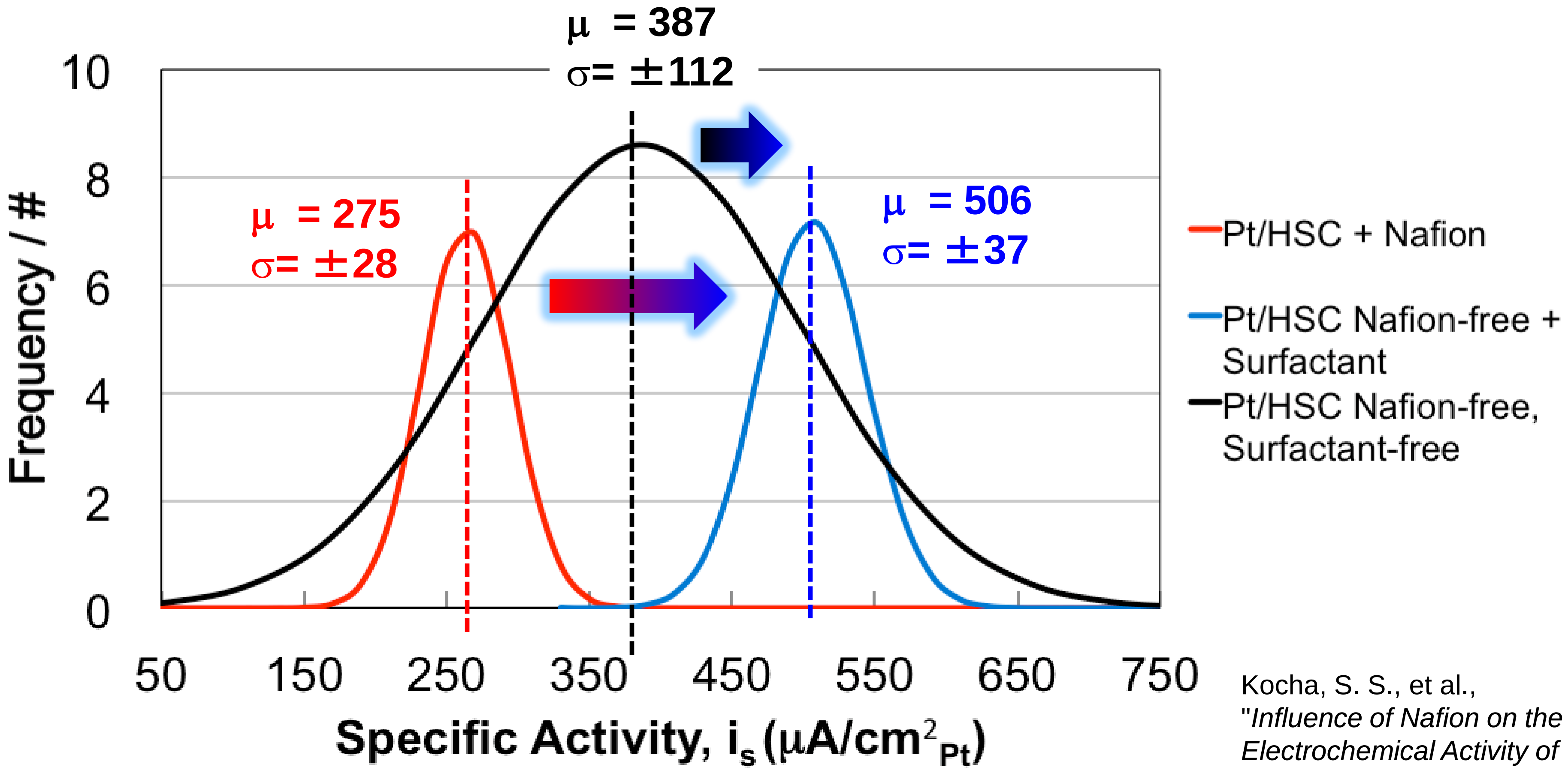


Based on ~45 individual sample measurements

Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

Wide distribution of activity values observed. Gaussian (Normal) distribution applied to obtain fits to the data.

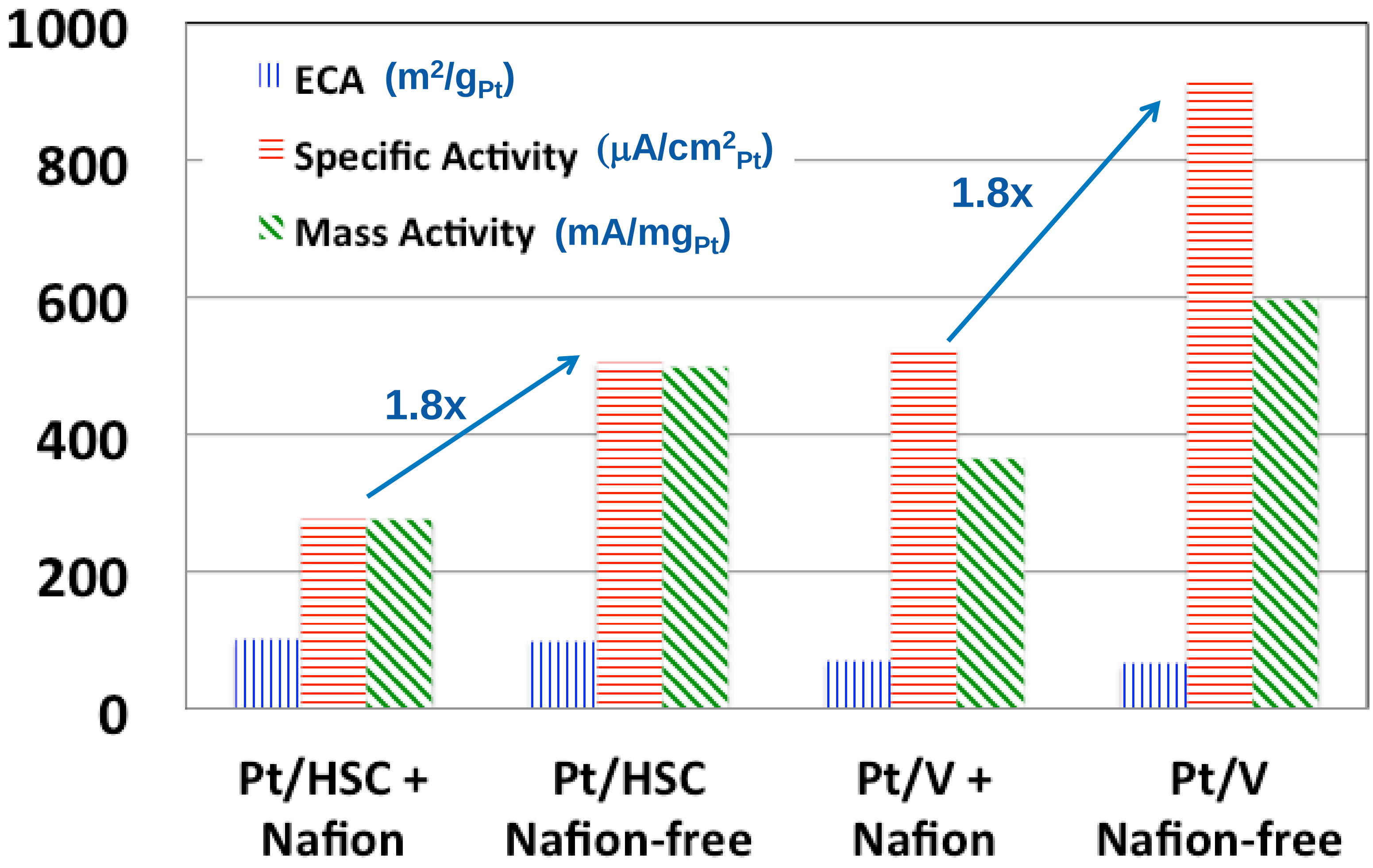
Pt/HSC: Nafion-based vs. Nafion-free vs. Nafion-free + Surfactant



Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

Statistically significant increase in activity for Nafion-free vs. Nafion-based Pt/HSC electrocatalyst.

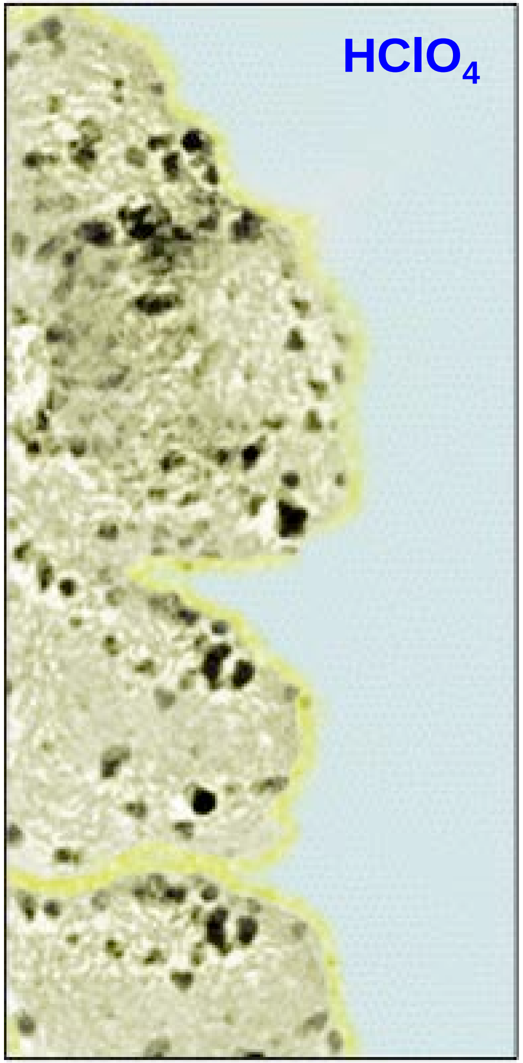
Summary of Results—Pt/HSC & Pt/Vulcan



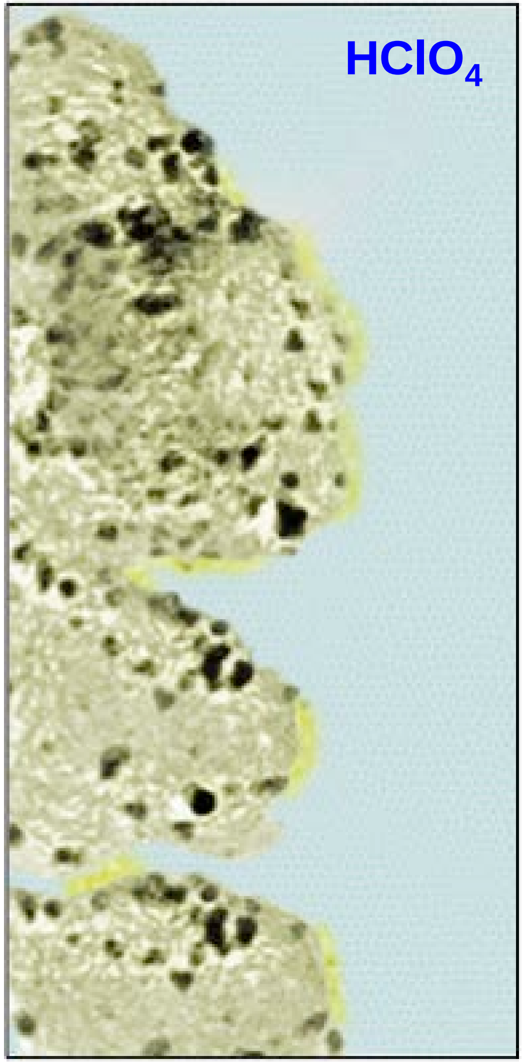
1.8x higher activity observed for Nafion-free Pt/C over Nafion based Pt/C.

Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

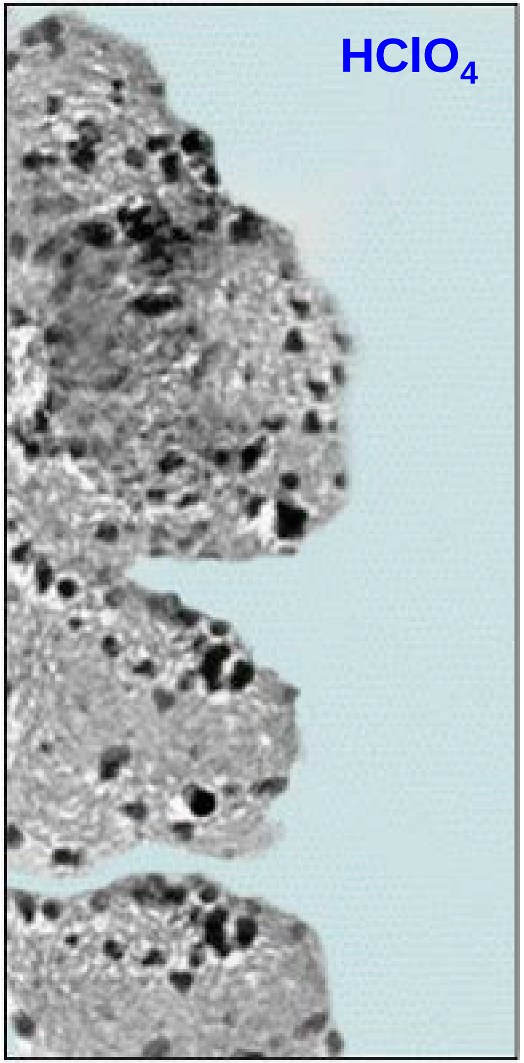
Hypothesis: Pt|C|Nafion|Acid Electrolyte Interface



Thick film



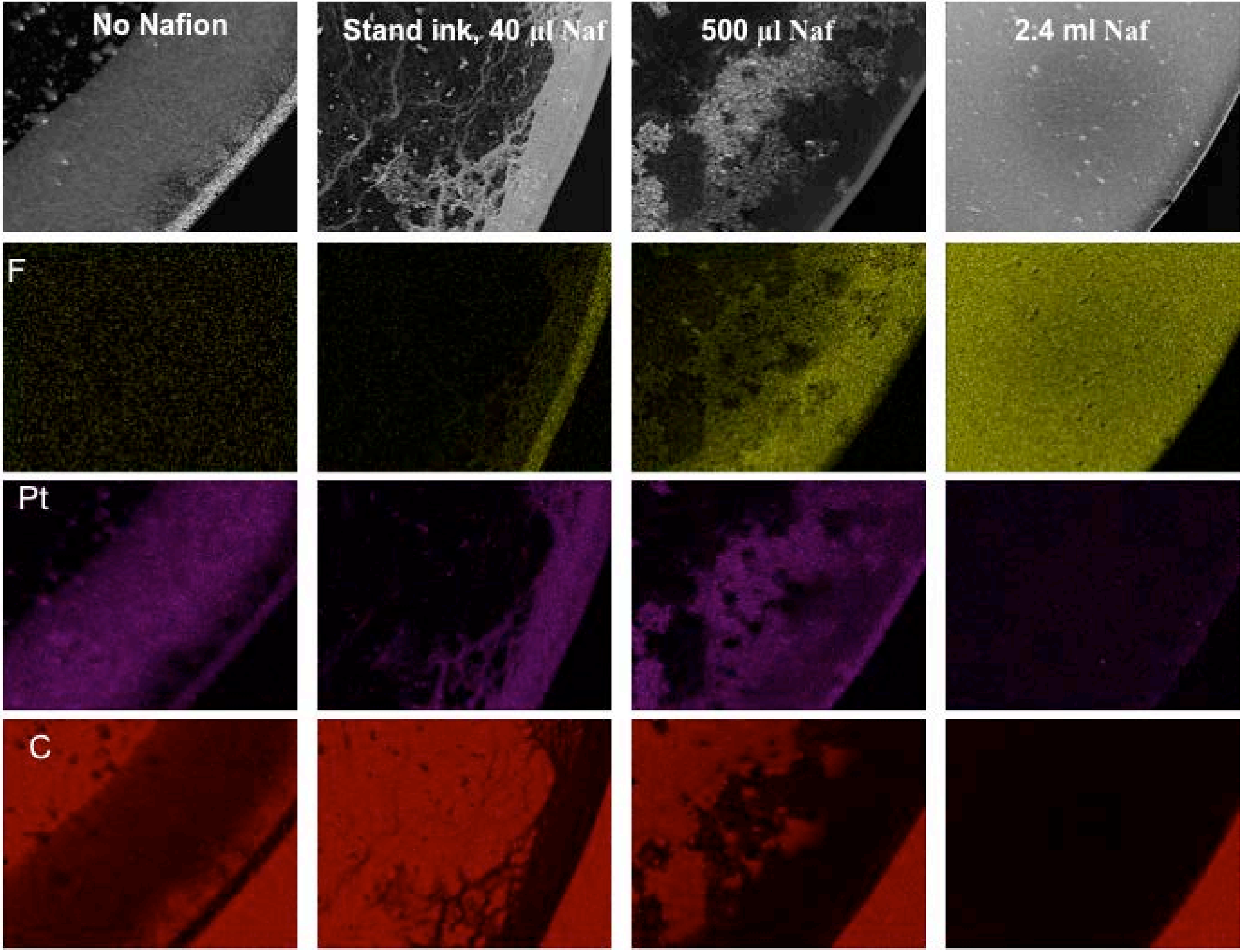
Patchy film



No ionomer

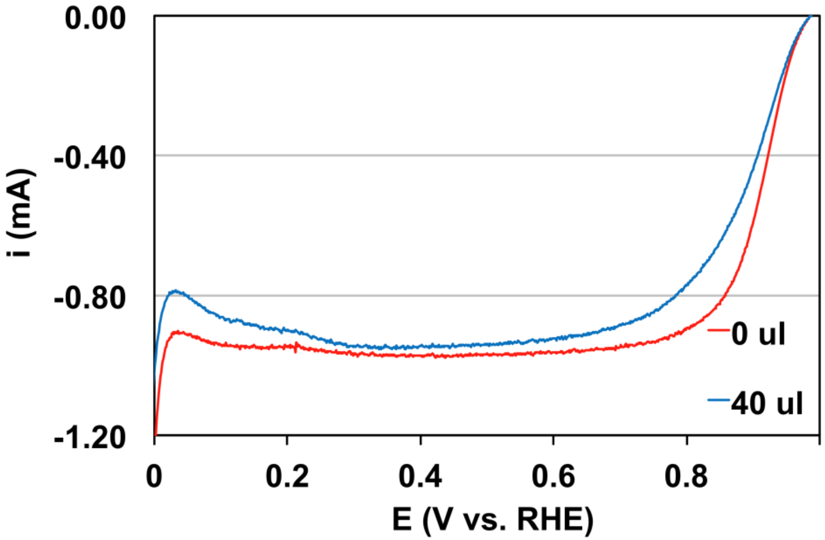
Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

SEM Micrographs: Elemental Analysis



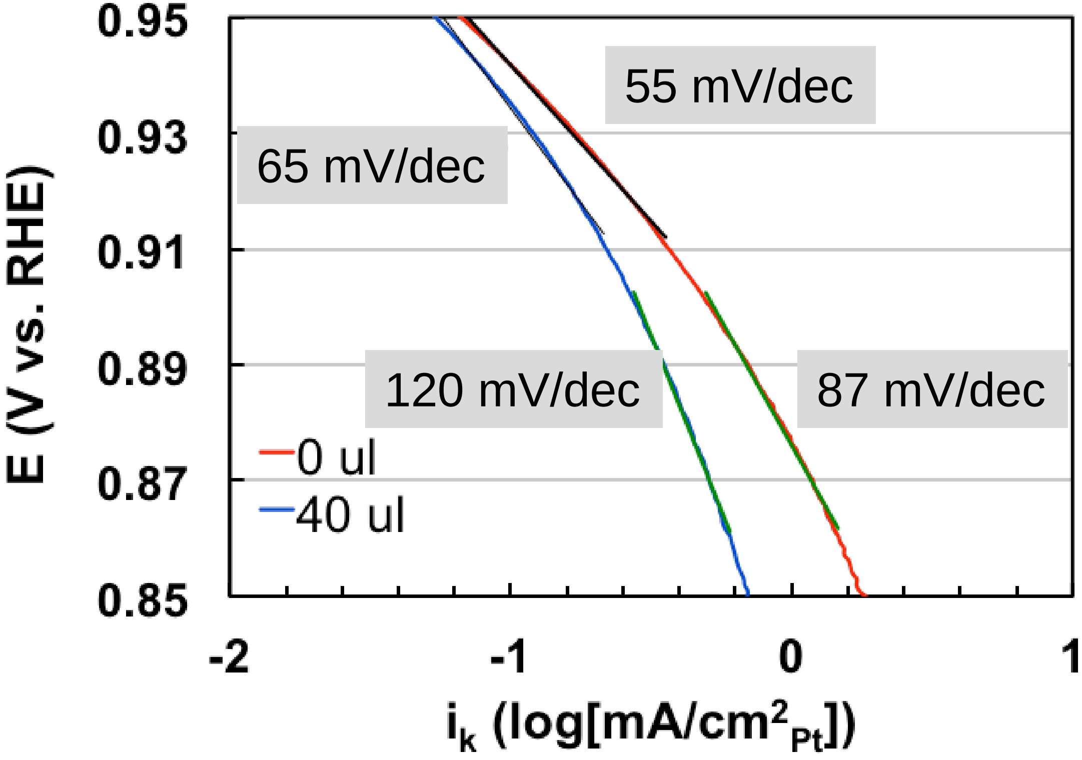
Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

Mass Transport: IVs and Tafels



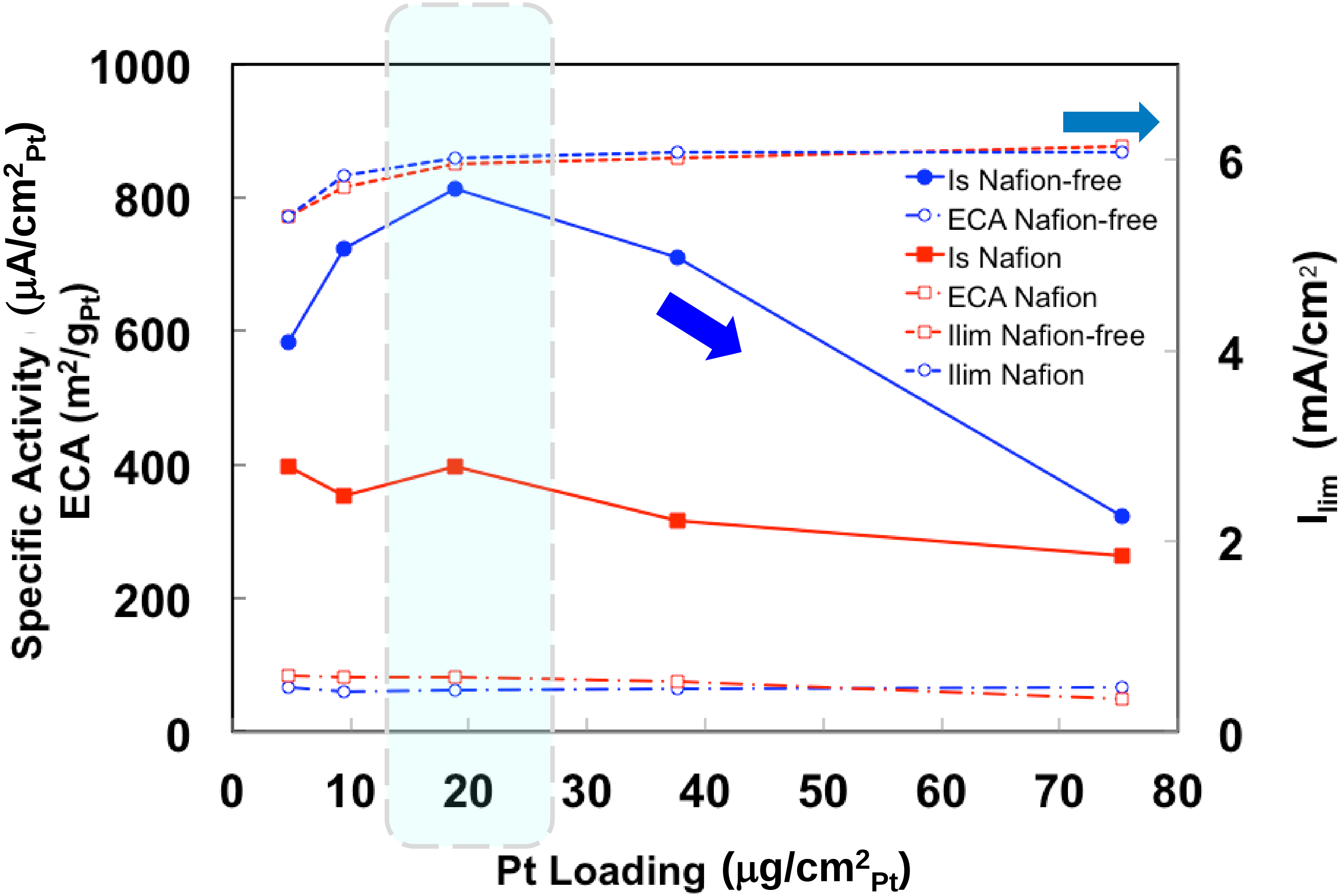
Raw I-V Curves for Pt/HSC with 40 μl of Nafion & Nafion- free (0 μl)

E vs. logi plots for Pt/HSC with 40 μl of Nafion & Nafion-free (0 μl)



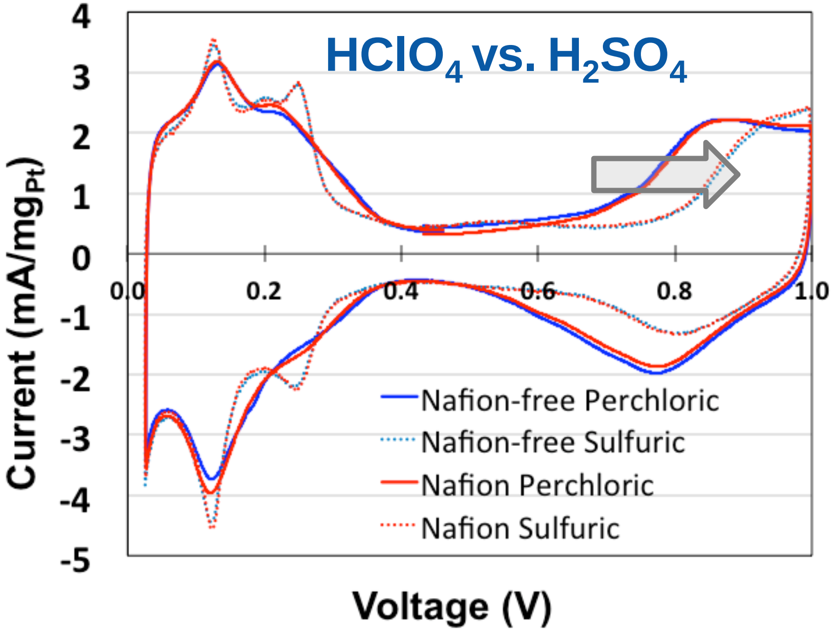
Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

Effect of Pt Loading (catalyst layer thickness)



Specific activity decreases with loading and thickness due to poorer O_2 diffusion.

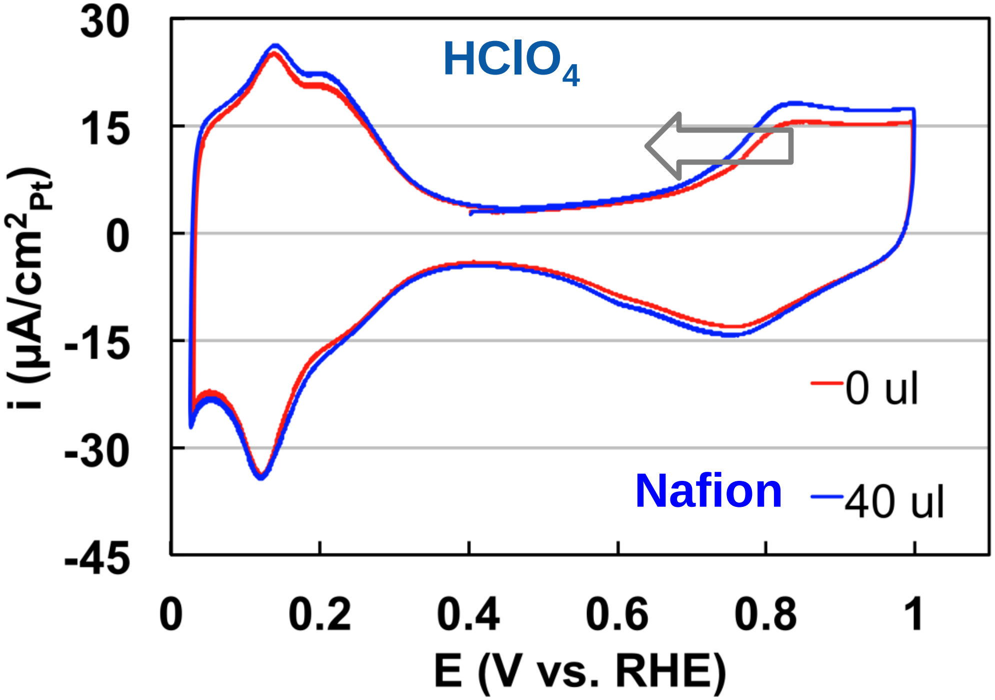
Anion Adsorption



Positive shift of oxide onset due to SO_4^- adsorption

Effect of sulfate anion adsorption on Nafion-based and Nafion-free Pt/HSC.

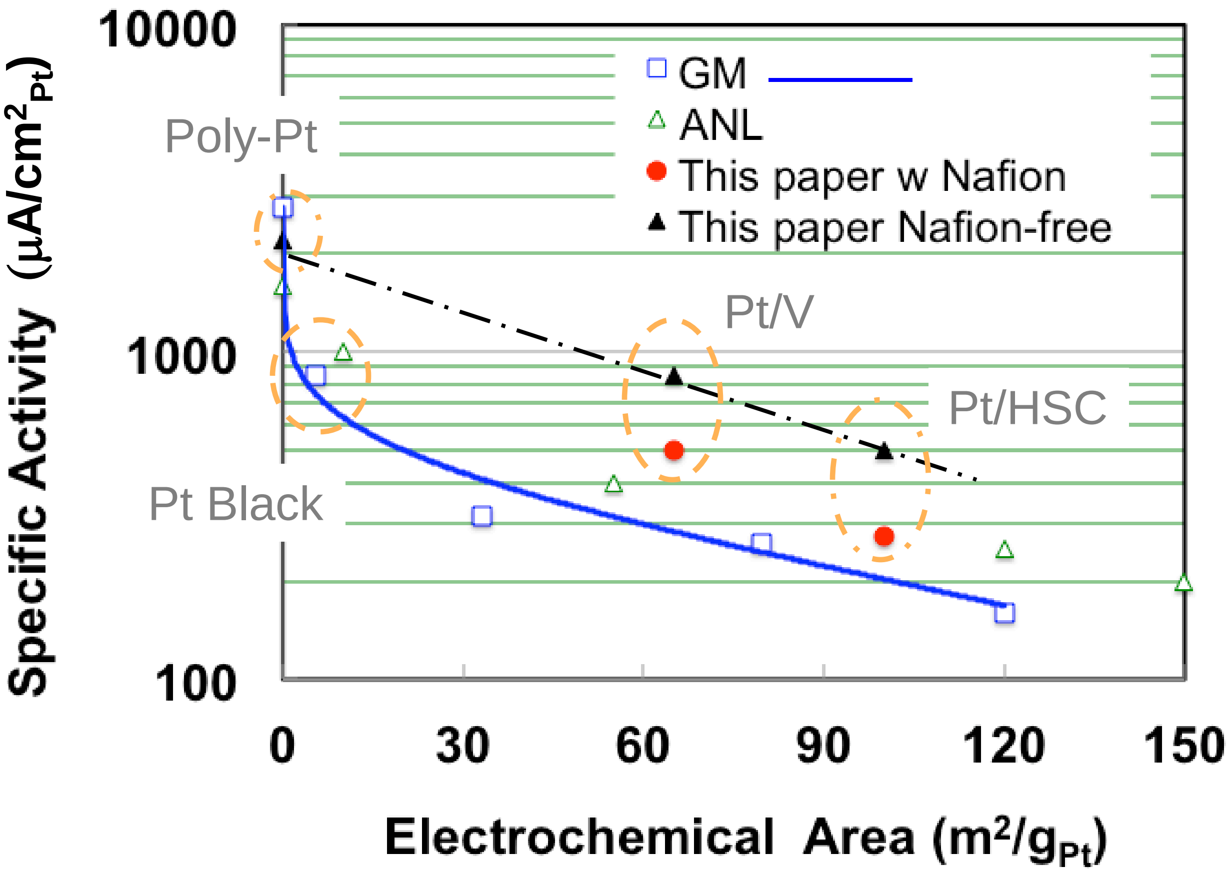
Slight negative shift of oxide onset



Effect of Sulfonate Adsorption

Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

Implications for 'Particle Size Effects'



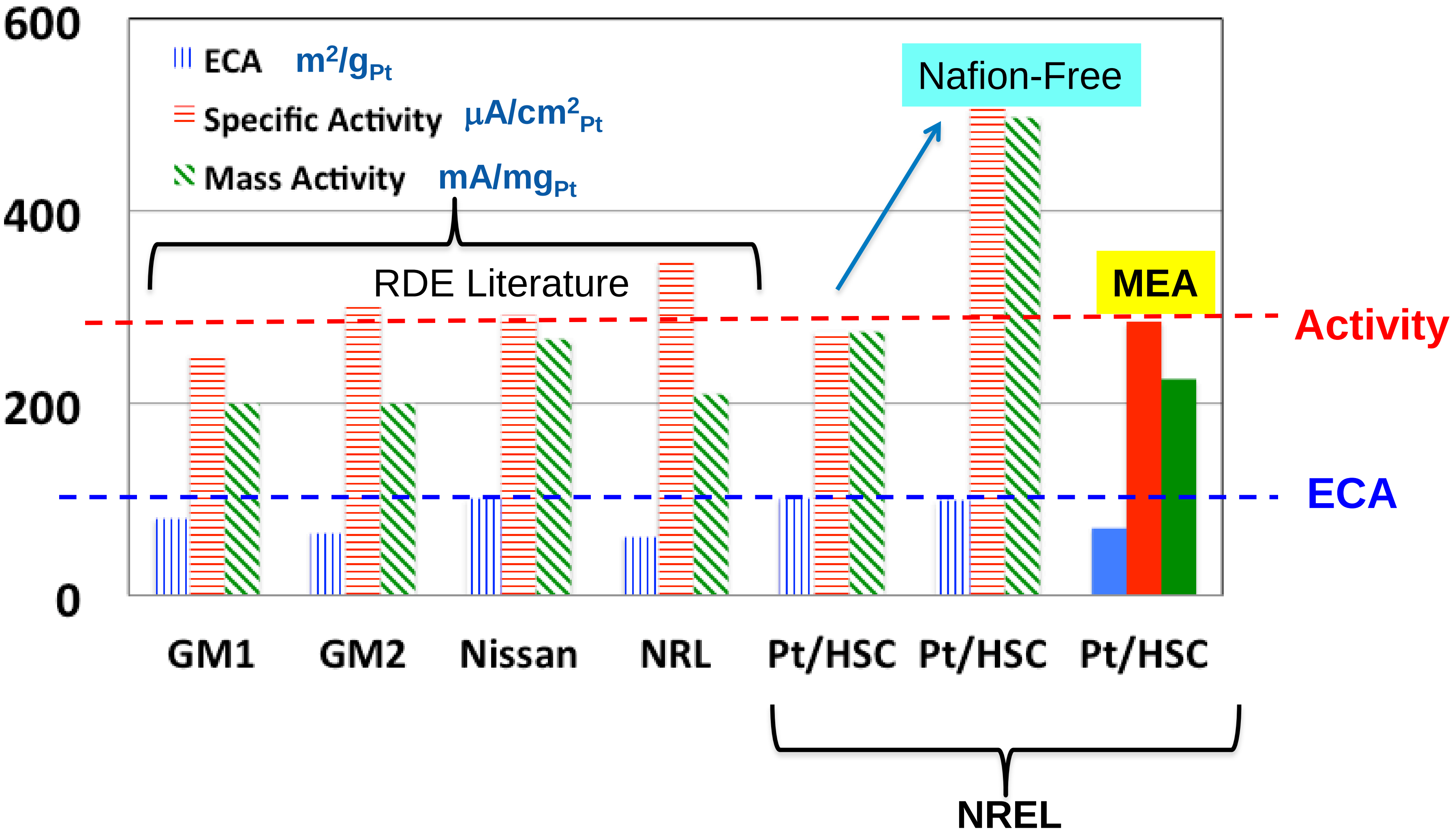
K. J. J. Mayrhofer, et al., *Electrochim. Acta*, **53**, 3181 (2008).

H. A. Gasteiger, S. S. Kocha, et al. *Appl. Catal. B-Environmental*, **56**, 9 (2005).

'Particle size effect' on specific activity (Pt/C in $HClO_4$) is **suppressed in the absence of Nafion** in electrodes.

Kocha, S. S., et al., "*Influence of Nafion on the Electrochemical Activity of Pt-based Electrocatalysts.*" ECS Trans. 2012, **50**.

Existing Pt/C Benchmarks: RDE–MEA



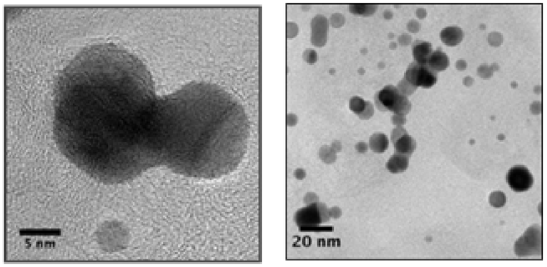
Benchmarks for ECA and Activity of Pt/HSC in RDE and PEMFC MEAs.

Kocha, S. S., et al., ." ECS Trans. 2012, **50**.

Durability Measurements in RDE

Considerations for RDE Durability Measurements

Loss of electrochemically-active surface area (ECA) and ORR activity

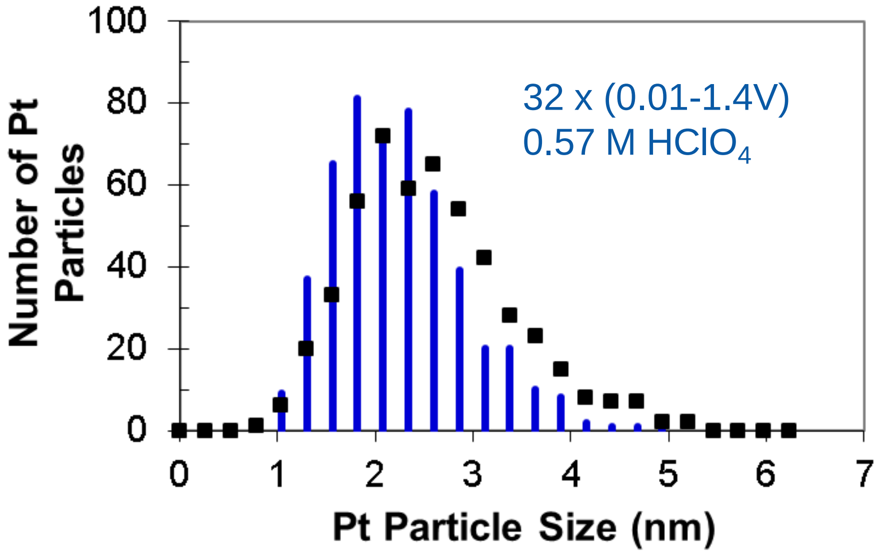


Images courtesy of Paulo Ferreira, UTexas-Austin

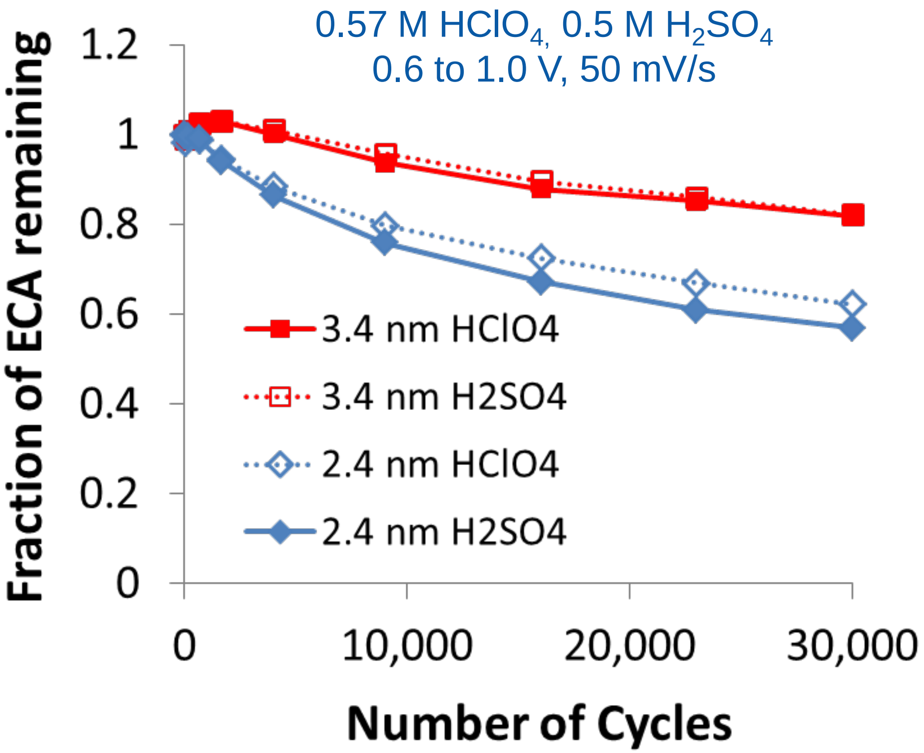
- ECA loss and particle size increases caused by:
  - Preferential dissolution preferentially of small particles <3.5 nm
  - Re-deposition onto larger particles
  - Re-deposition between particles to coalesce particles
  - Corrosion of support with loss of electronic contact or particle coalescence
- Extent of ECA loss and evolution of PSD will depend on the extent of contributions from these four mechanisms
- Extent of dissolution and re-deposition and corrosion of support will depend on:
  - Upper and lower potential limits of cycling, profile, and scan rate
  - Transport of dissolved Pt away from electrode (e.g., by rotation)
  - ECA to solution volume ratio
  - Temperature

Factors Affecting RDE Durability Measurements

- Cycling in 0.57 M $HClO_4$ and 0.5 M H_2SO_4 results in similar loss of ECA
- ECA loss increases with increasing temperature
- Considerable change in PSD and particle surface area can occur during “conditioning”

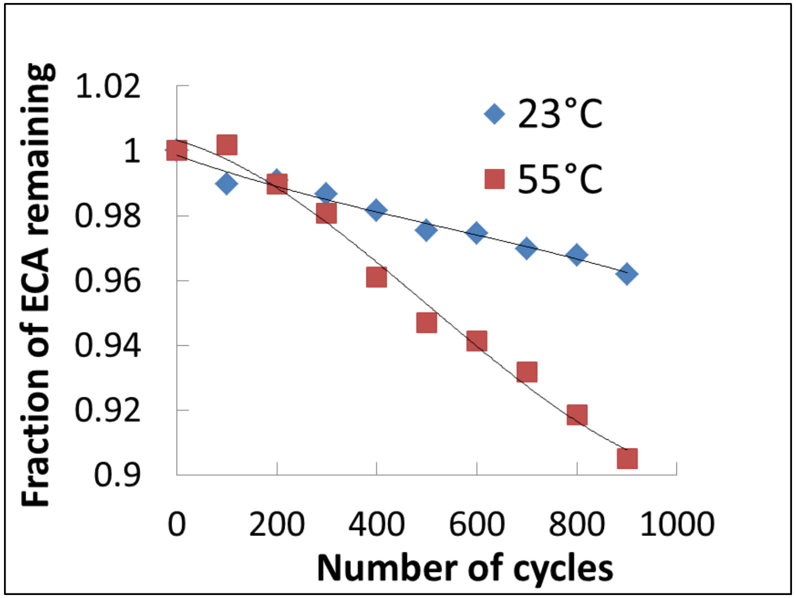


32 x (0.01-1.4V)
0.57 M $HClO_4$



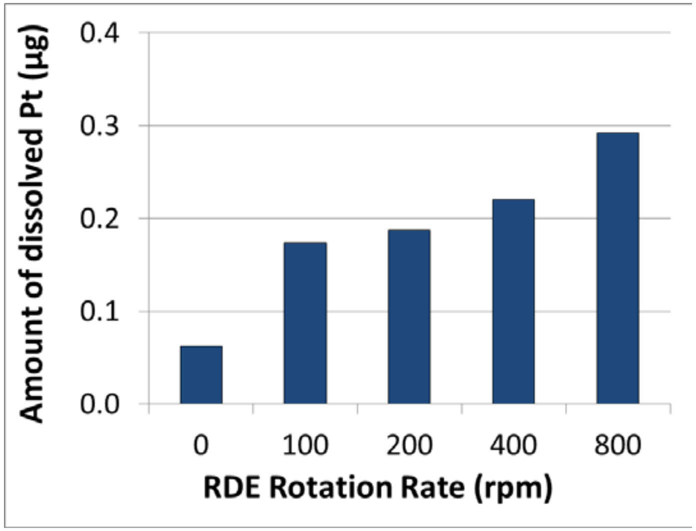
0.57 M $HClO_4$, 0.5 M H_2SO_4
0.6 to 1.0 V, 50 mV/s

0.1 M $HClO_4$, 0.4 to 1.05 V square, 20 s/cycle

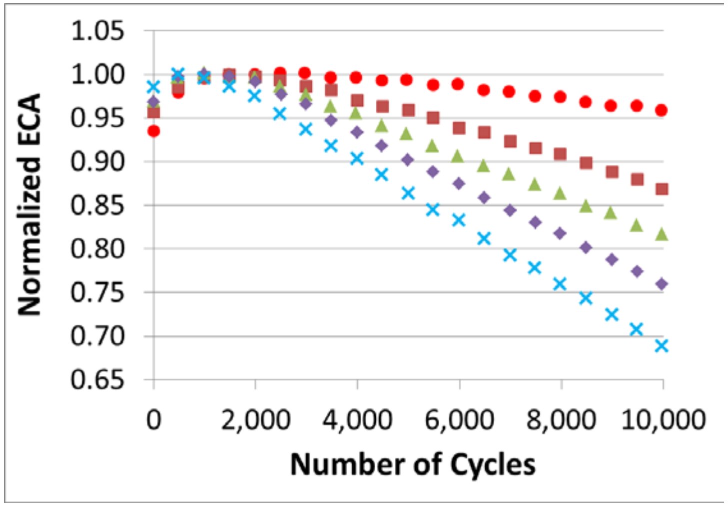


ECA loss and dissolved Pt concentration

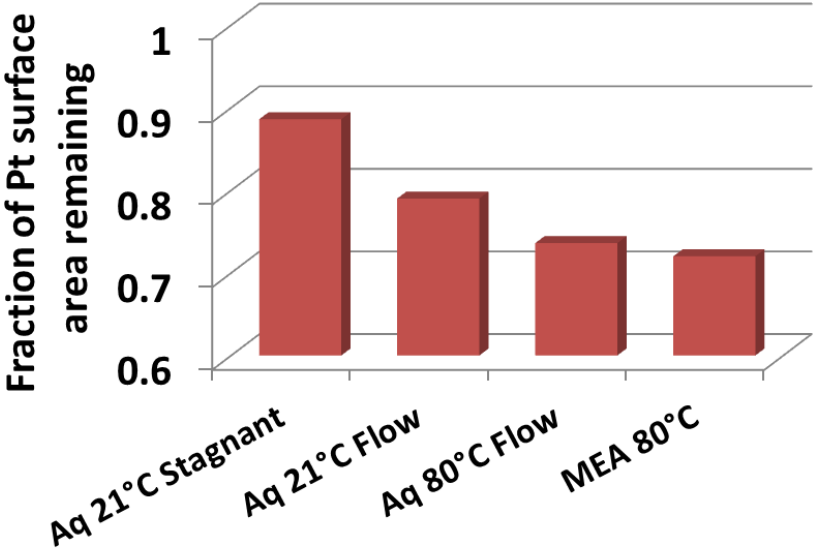
Data in two upper plots courtesy of Y. Morimoto: T. Nagai, M. Murata, and Y. Morimoto, Honolulu PRiME 2012, The Electrochemical Society, Oct. 2012, Abstract No. 1320



0.4 to 1.1 V Steps

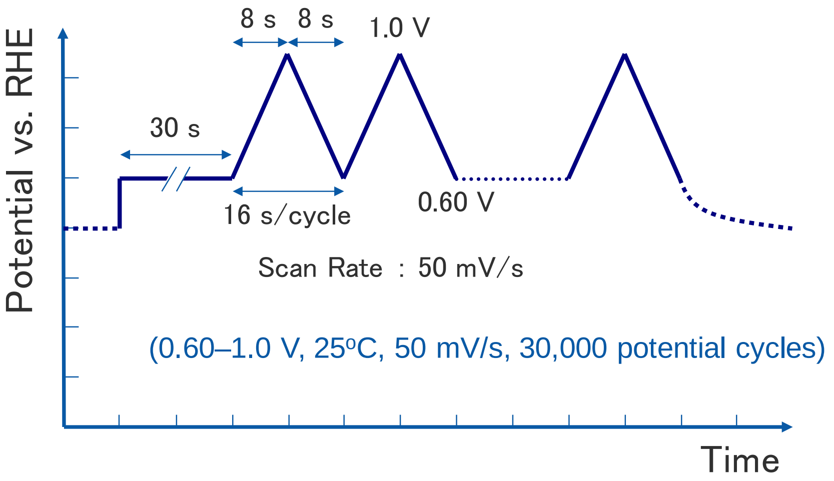


- Aqueous electrolyte allows determination of catalyst component dissolution rates
- ICP-MS analysis of dissolved Pt concentration (1 ppt dl for high-resolution ICP-MS)
- Dissolved Pt concentration and ECA loss increase with increasing rotation rate due to increased dissolution and decreased re-deposition
- Elevated temp. and rotation or flow approximate MEA ECA losses



Durability Protocols for PGM Catalysts and Supports

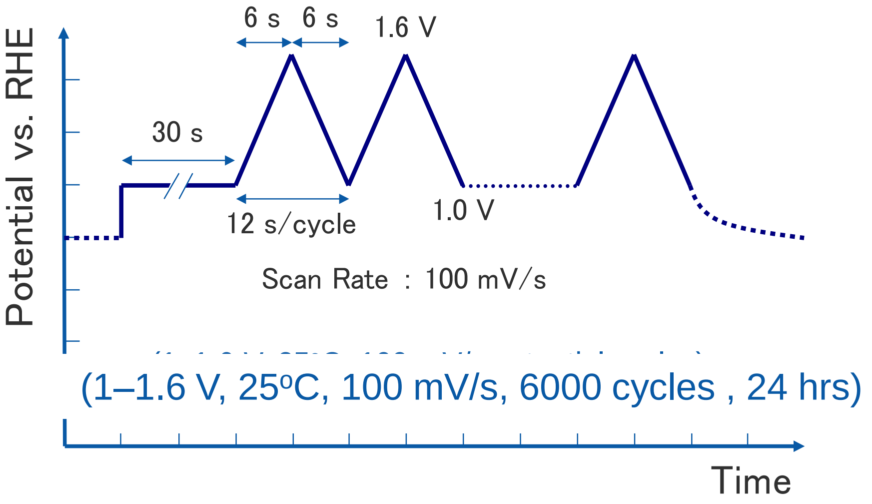
Catalyst Protocol



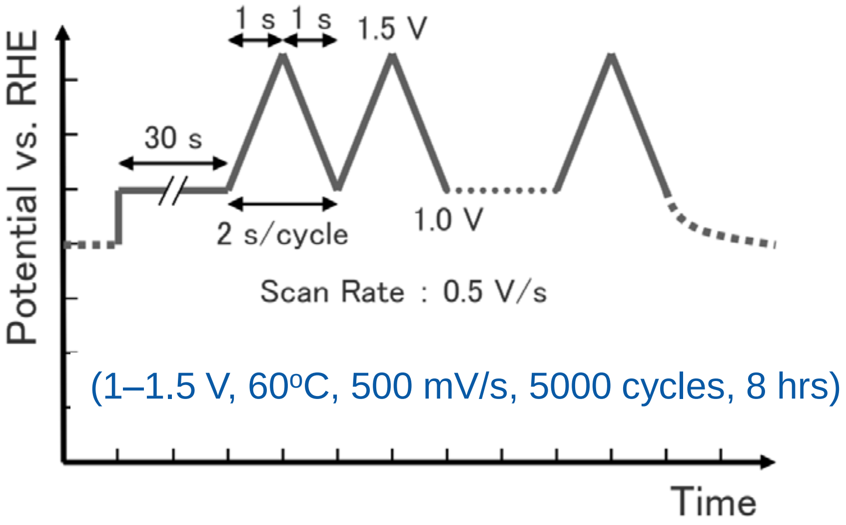
(0.60–1.0 V, 25^{o}C, 50 mV/s, 30,000 potential cycles)

- **Diagnostic measurements:**
  - ECA, ORR specific and mass activities
  - After 10, 100, 1k, 3k, 10k, 20k and 30k cycles
- **Parameters to be reported:**
  - Electrolyte type, concentration, temperature, rotation rate during cycling
  - Method used for ECA measurement and constant used for calculating ECA
  - Scan rate and direction for ORR measurement, rotation rate, reference electrode used and method for converting to RHE scale

Support Protocol



(1–1.6 V, 25^{o}C, 100 mV/s, 6000 cycles , 24 hrs)



(1–1.5 V, 60^{o}C, 500 mV/s, 5000 cycles, 8 hrs)

Summary

RDE techniques are suitable for evaluating/screening the ECA and electrochemical activity and durability of small quantities of novel electrocatalysts for PEMFCs.

A number of factors influence the measured activity including:

—Measurement protocol used for testing

—Operating conditions

—Ink formulation

—Film deposition

Further work needs to be done in combining the best practices and to approach the “true activity” of electrocatalysts.

In the interest of being able to easily compare results found in the literature, it would be helpful if a standard test protocol (example: slide 10) is established.

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Next Step

DOE plans to solicit input from stakeholders and the research community, most likely via the release of a Request for Information (RFI) later this year, on a standard RDE test protocol

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https://www1.eere.energy.gov/hydrogenandfuelcells/webinars.html

Additional References

F. Gloaguen, F. Andolfatto, R. Durand and P. Ozil, J. Appl. Electrochem., **24**, 863 (1994).

T. J. Schmidt, H. A. Gasteiger, O. D. Staeb, P. M. Urban, D. M. Kolb and R. J. Behm, J. Electrochem. Soc., **145**, 2354 (1998).

U. A. Paulus, T. J. Schmidt, H. A. Gasteiger and R. J. Behm, J. Electroanal. Chem., **495**, 134 (2001).

E. Claude, T. Addou, J.-M. Latour and P. Aldebert, J. Appl. Electrochem., **28**, 57 (1998)

V. R. Stamenkovic, B. S. Mun, M. Arenz, K. J. J. Mayrhofer, C. A. Lucas, G. Wang, P. N. Ross and N. M. Markovic, Nature Materials, **6**, 241 (2007).

K. J. J. Mayrhofer, D. Strmcnik, B. B. Blizanac, V. Stamenkovic, M. Arenz and N. M. Markovic, Electrochim. Acta, **53**, 3181 (2008).

R. R. Adzic, J. Zhang, K. Sasaki, M. B. Vukmirovic, M. Shao, J. X. Wang, A. U. Nilekar, M. Mavrikakis, J. A. Valerio and F. Uribe, Topics in Catalysis, **46**, 249-262 (2007).

B. Merzougui and S. Swathirajan, J. Electrochem. Soc., **153**, A2220 (2006).

S. S. Kocha, *Electrochemical Degradation: Electrocatalyst and Support Durability*. **Chapter 3** in Polymer Electrolyte Fuel Cell Degradation, Editors: M. Mench, E.C. Kumbur, T. N. Veziroglu, p. 89–185,(2011).

H. A. Gasteiger, S. S. Kocha, B. Sompalli and F. T. Wagner, Applied Catalysis B-Environmental, **56**, 9-35 (2005).

I. Takahashi and S. S. Kocha, Journal of Power Sources, **195**, 6312-6322 (2010).

Y. Garsanny, I. L. Singer and K. E. Swider-Lyons, J. Electroanal.Chem., **662**, 396 (2011).

S. S. Kocha, *Principles of MEA Preparation*, in: W. Vielstich, A. Lamm and H. Gasteiger (Eds.), Handbook of Fuel Cells-Fundamentals, Technology and Applications, vol 3 **Chapter 43**, John Wiley & Sons, Ltd., p. 538-565 (2003).

Y. Garsany, O. A. Baturina, K. E. Swider-Lyons and S. S. Kocha, Anal. Chem., **82**, 6321-6328 (2012).

L. J. Bregoli, Electrochim. Acta, **23**, 489-492 (1978).

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