V.M.1 Best Practices and Benchmark Activities for ORR Measurements by the Rotating Disk Electrode Technique

Shyam S. Kocha[1] (Primary Contact), Jason W. Zack,[1] Kazuma Shinozaki,[1] Svetlana Pylypenko,[1] Vojislav Stamenkovic[2] (co-PI), Yijin Kang,[2] Dongguo Li,[2] Deborah Myers[3] (co-PI), Nancy Kariuki,[3] Tammi Nowicki[3]
National Renewable Energy Laboratory[1]
Fuel Cell Group
Phone: (303) 275-3284
Email: shyam.kocha@nrel.gov
Argonne National Laboratory (ANL)[2]
Energy Conversion and Storage Group
Argonne National Laboratory[3]
(Hydrogen and Fuel Cell Materials Group)

DOE Manager
David Peterson
Phone: (720) 356-1747
Email: David.Peterson@ee.doe.gov

Project Start Date: October 1, 2013
Project End Date: September 30, 2014

Overall Objectives

To aid DOE by establishing protocols and best practices for rotating disk electrode (RDE) measurements which would allow for more reliable oxygen reduction reaction (ORR) activity comparisons to be made in the area of electrocatalyst development.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability and (C) Performance

- Best practices/protocol for electrocatalyst screening not standardized
- Benchmark activity for baseline Pt/C electrocatalysts for comparison to novel electrocatalysts not available
- Common/standard Pt/C catalysts not accessible
- Reproducibility of results

Fiscal Year (FY) 2014 Accomplishments

- Established a standard protocol and test methodology for measurement of electrochemical area (ECA), ORR activity, and durability.
- Evaluated three electrocatalysts using identical protocols and electrode preparation in three laboratories for ECA, ORR activity.
- Compared and verified ECA, ORR activity and durability for reproducibility between labs.

✧ ✧ ✧ ✧ ✧

INTRODUCTION

The need for large amounts of materials and the complexity and cost of fabricating fuel cells have led to the widespread use of RDE measurements in aqueous acidic electrolyte to study the activity and stability of nano-materials used in proton exchange membrane fuel cell electrode catalysts. In addition to eliminating the need to fabricate membrane electrode assemblies (MEAs), as the first step in the catalyst evaluation process, RDE measurements also allow precise control over the potential of the fuel cell nano-catalysts and eliminate the influence of other cell components, such as the membrane, gas diffusion layer, and the opposing electrode on the initial performance and performance decay of the nano-catalyst of interest.

Several groups over the last few years have reported discrepancies in activity values reported between research groups and also improvements in technique that allowed for higher and more reproducible activity [1-3]. DOE worked with NREL and ANL to issue a Request for Information (RFI) on best practices for RDE measurements for ORR activity. The purpose of the RFI was to solicit feedback from catalyst developers, researchers, manufacturers, end users, and other stakeholders on use of RDE experiments for characterization/screening of the activity and durability of proton exchange membrane fuel cell electrocatalysts. DOE also organized a webinar on RDE to disseminate preliminary information and solicit input on RDE testing [5]. Lastly, the Catalysis Working Group (CWG) and Durability Working Group (DWG) joint meeting was held at NREL with one of the objectives being the discussion of responses to the RDE RFI [6]. The overarching goal is to develop best practices/protocols to enable consistency in procedures and minimize variability in results from different laboratories so that novel catalysts can be accurately benchmarked.

APPROACH

Our approach is to establish protocols and best practices for ink dispersion/film deposition/drying for 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.

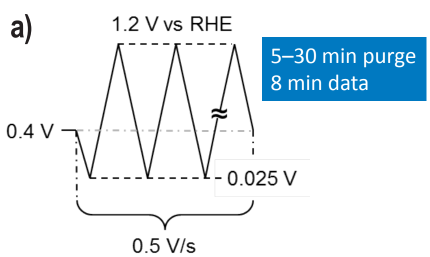
Briefly, the approach involves obtaining electrocatalytic activity measurements for:

- 2–3 commercially obtainable Pt/C electrocatalysts
- in which the activity is measured for a high degree of statistical reproducibility
- with the same protocol and ink formulation and having the catalysts tested in three laboratories

RESULTS

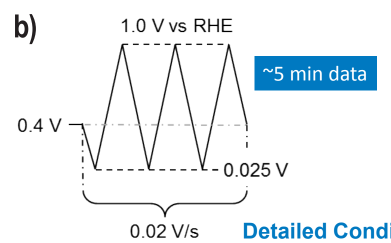
Protocols were established based on a large number of experiments conducted at NREL and based on discussions with the CWG and DWG and responses to the DOE RFI on RDE testing [6]. A number of sources for perchloric acid was also evaluated to determine the grades that had the least amount of impurities that contaminate platinum catalysts. The schematic and details of the conditioning, ECA and ORR activity protocols are detailed in Figure 1 a), b), and c). These protocols were used as a standard for all studies. The Pt/C catalyst specifications obtained from the three manufacturers is detailed in Figure 2.

Poly-Pt was used as a sensor of the cleanliness of the RDE electrochemical cell prior to conducting measurements on the three electrocatalysts from three catalyst suppliers (TKK, JM, Umicore) in three laboratories (NREL and two labs at ANL). The average ORR activity of poly-Pt at NREL was found to be 2.80 mA/cm^2_{Pt} ± 0.20 and are comparable to some of the highest values reported in the literature. A specific activity of poly-Pt that was greater than ~2.0 mA/cm^2_{Pt} was found to be necessary in order to qualify the cell as having impurity levels below an acceptable limit in which the ORR activity of Pt-based catalysts could be measured with reasonable accuracy. Furthermore, the



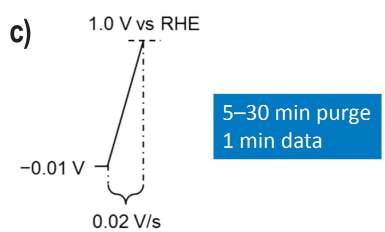
Detailed Conditions

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



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



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)

FIGURE 1. a) Schematic and details of conditioning protocol; b) Schematic and details of ECA protocol; c) Schematic and details of ORR activity protocol.

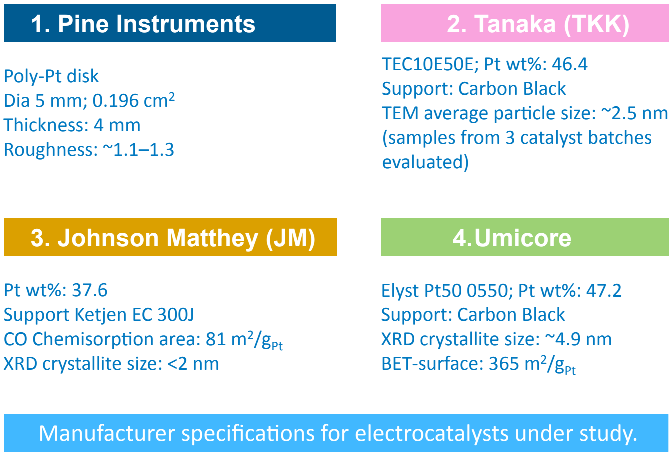


FIGURE 2. Pt/C specifications from catalyst maufacturers.

activity of poly-Pt was found to be invariant for about an hour of repeated cycling (not shown). Figure 3 compares the ORR activity of poly-Pt measured in the three laboratories. Note that different electrochemical cells were employed at the three laboratories, but identical protocols and electrode surface preparations were employed.

Subsequently, using identical standardized protocols (Figure 1) and a standardized electrode preparation method of spin coating [2-3] two of the three electrocatalyst materials from TKK, JM, and Umicore were evaluated in the three laboratories. A comparison of the ORR mass activity between laboratories for the two catalysts indicates acceptable reproducibility as shown in Figure 4.

CONCLUSIONS AND FUTURE DIRECTIONS

- A standard RDE testing protocol and standard electrode preparation method were deveioped for making RDE measurements relevant for PEM fuel cell cathode electrocatalysis development. These techniques were verified and found to be reproducible across three laboratories.
- Finalize a strategy on the logistics of potentially distributing/shipping ~1 g of electrocatalyst material (no charge) to those groups that are awarded a new electrocatalyst related project in upcoming DOE Funding Opportunity Announcements over the next 5 years.
- Disseminate the results of the study (best practices for RDE and benchmark activity values) so that it is accessible to the scientific community and the general public.

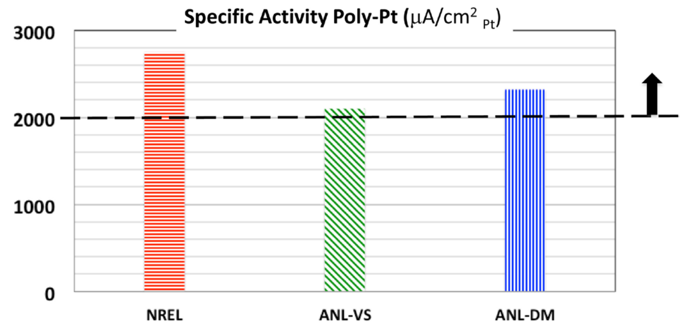


FIGURE 3. Comparison of specific activity between laboratories of poly-Pt in 0.1M $HClO_4$ at 25°C and 100 kPa conducted at 20 mV/s in the anodic sweep.

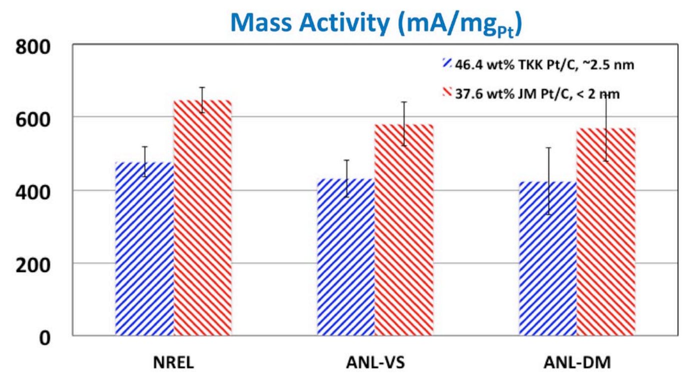


FIGURE 4. Comparison of mass activity between laboratories of 2 Pt/C electrocatalysts in 0.1M $HClO_4$ at 25°C and 100 kPa conducted at 20 mV/s in the anodic sweep.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Kocha, Shyam S., Jason W. Zack, Shaun M. Alia, K.C. Neyerlin, and Bryan S. Pivovar. "Influence of Ink Composition on the Electrochemical Properties of Pt/C Electrocatalysts." ECS Transactions 50, no. 2 (2013): 1475-1485.

2. Garsany, Yannick, Irwin L. Singer, and Karen E. Swider-Lyons. "Impact of film drying procedures on RDE characterization of Pt/VC electrocatalysts." Journal of Electroanalytical Chemistry 662, no. 2 (2011): 396-406.

3. Shinozaki, Kazuma, Bryan S. Pivovar, and Shyam S. Kocha. "Enhanced Oxygen Reduction Activity on Pt/C for Nafion-free, Thin, Uniform Films in Rotating Disk Electrode Studies." ECS Transactions 58, no. 1 (2013): 15-26.

4. Catalysis Working Group (CWG) and Durability Working Group (DWG) Meetings, Co-Chairs: Piotr Zelenay, Nancy Garland and Deborah Myers, Rod Borup, presented by Kocha, S.S. "Influence of Ink Composition on the Electrochemical Properties of Pt/C Electrocatalysts." Honolulu, Hawaii, 2012.

5. DOE Webinar: Shyam S. Kocha, Yannick Garsany, Deborah Myers, Chair: Dimitrios Papageorgopoulos, 'Testing Oxygen Reduction Reaction Activity with the Rotating Disc Electrode. Technique', http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/webinarslides_rde_technique_031213.pdf.

6. Catalysis Working Group (CWG) meeting and Durability Working Group (DWG) meeting at NREL/DOE Field Office, December 2013.