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pH matters: The influence of the catalyst ink on the oxygen reduction activity determined in thin film rotating disk electrode measurements

Masanori Inaba [a, b], Jonathan Quinson [a], Matthias Arenz [a, c, *]

[a] Nano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100, Copenhagen Ø, Denmark
[b] Toyota Central R&D Labs., Inc., Nagakute, Aichi, 480-1192, Japan
[c] Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012, Bern, Switzerland

HIGHLIGHTS

- Impact of catalyst ink pH on ORR activity determined by Tf-RDE was investigated.
- A significant increase in ORR activity is seen increasing the pH of the catalyst ink.
- The dispersion of the catalyst ink improves with increasing ink pH.
- The mass transfer resistance through catalyst film decreases with increasing ink pH.
- The catalyst ink pH needs to be considered when evaluating catalysts by RDE.

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ABSTRACT

We investigated the influence of the ink properties of proton exchange membrane fuel cell (PEMFC) catalysts on the oxygen reduction reaction (ORR) activity determined in thin film rotating disk electrode (TF-RDE) measurements. It was found that the adaption of a previously reported ink recipe to home-made catalysts does not lead to satisfying results, although reported work could be reproduced using commercial catalyst samples. It is demonstrated that the pH of the catalyst ink, which has not been addressed in previous TF-RDE studies, is an important parameter that needs to be carefully controlled to determine the intrinsic ORR activity of high surface area catalysts.

1. Introduction

Rotating disk electrode (RDE) measurements are a popular approach to test the performance of electrocatalysts in so-called electrochemical half-cell measurements [1–5]. Originally the method was developed for planar electrodes, where it enables defined mass transport conditions of a reactant that is dissolved in the electrolyte to the electrode surface. Using hydrodynamics, it is then possible to extract the “kinetics” from the measured current densities. One of the main assumptions for such a kinetic analysis, see Ref. [6] for details, is that the mass transport to each point of the catalyst surface is identical.

With increasing interest in proton exchange membrane fuel cells (PEMFCs) there was a need for a fast reliable method to screen-test different catalysts, especially for the oxygen reduction reaction (ORR), the cathode process in PEMFCs. This need was addressed by applying a thin catalyst layer onto glassy carbon (GC) electrodes in a RDE configuration, the so-called thin-film (TF-) RDE method [1]. The TF-RDE method became extremely popular in PEMFC research and is now used as standard to compare different catalysts, and not least to substantiate claims of critical activity improvements.

However, as discussed in the work by Gasteiger et al. [2], the need for benchmarking catalysts became apparent with the comparison of activities reported by different groups: for similar catalysts, differences in ORR activities of one order of magnitude were reported. Such variations are indeed critical not only as they prove that comparisons to the literature are difficult; but because they

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* Corresponding author. University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland.
E-mail address: matthias.arenz@dcb.unibe.ch (M. Arenz).

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also pose the question of the “real” intrinsic ORR activity of Pt catalysts.

Since then several groups worked on procedures to systematically analyze the ORR activity of fuel cell catalysts from TF-RDE measurements [3,7–13]. Especially, during the last few years, the influence of catalyst layer quality on measured ORR activity and its reproducibility has been highlighted. Several thin film fabrication approaches to obtain homogeneous catalyst layers were reported [11–13], showing that the optimization of the catalyst ink properties and the film drying method play a key role in the assessment of ORR activities of high surface area catalysts.

Most recently, researchers at the national renewable energy laboratory (NREL) characterized catalyst films fabricated by using several ink formulations and film-drying techniques [5]. According to their report, the highest quality films (based on homogeneity assessed by microscopy techniques as well as resulting ORR activity values) for a commercial TKK 46 wt % Pt/C catalyst were obtained with high reproducibility by adding isopropanol (IPA) (25% in volume ratio) to a catalyst ink containing only pure water and the Pt/C catalyst powder followed by drying the ink on GC electrodes in an IPA atmosphere (Nafion-free stationary IPA drying (NF-SIPAD) technique). The measured ORR specific activity (SA) from these catalyst films was significantly higher than the values reported in previous reports [2,8,12,14–17].

In the work presented here, we tried to adapt the reported ink recipe and film-drying method to home-made catalyst that were synthesized via a colloidal approach that aims at enabling systematic studies of high surface area catalysts [18]. Our results demonstrate that a direct transfer leads to inferior results as compared to using pure water to prepare the catalyst inks – although the reported findings could be reproduced. It is argued that, similar to the preparation of membrane electrode assemblies (MEAs) [19], the pH of the catalyst ink is an important parameter that needs to be carefully controlled when evaluating ORR activity of high surface area catalysts via the TF-RDE technique.

2. Experimental

2.1. Chemicals and gases

The following chemicals were used in the catalyst synthesis and characterization: ethylene glycol (EG, 99.8%, Sigma-Aldrich), sodium hydroxide (NaOH, 98.9%, Fisher Chemical), hexachloroplatinic(IV) acid hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, 99.9%, Alfa Aesar), 30% hydrochloric acid (HCl, Suprapur, Merck), 60% nitric acid (HNO_3, Suprapur, Merck) and acetone (99.5+ %, Alfa Aesar). Two kinds of commercial carbon black, Vulcan XC72R (Cabot Corporation, BET area: 235 $m^2\ g^{-1}$) and Ketjen EC-300J (AkzoNobel Polymer Chemistry, BET area: 795 $m^2\ g^{-1}$), were employed as carbon support in the catalyst synthesis. Deionized (DI) water (resistivity > 18.2 MΩ cm, total organic carbon (TOC) < 5 ppb) from a Milli-Q system (Millipore) was used for acid/base dilutions, catalyst ink formulation, and the electrochemical cell cleaning. Isopropanol (IPA, 99.7+ %, Alfa Aesar), 70% perchloric acid ($HClO_4$, Suprapur, Merck), and potassium hydroxide hydrate ($KOH \cdot H_2O$, Suprapur, Merck) were used for catalyst ink formulation and electrolyte preparation. The following gases from Air Liquide were used in electrochemical measurements: Ar (99.999%), O_2 (99.999%), CO (99.97%), and (H_2 99.999%).

2.2. Synthesis of 50 wt % Pt/C catalysts

50 wt % Pt/C electrocatalysts were synthesized via the tool-box approach we previously reported [18]. The synthesis method of the electrocatalyst consists of two main steps: a suspension of colloidal Pt nanoparticles (NPs) is prepared via an alkaline ethylene glycol (EG) route [20], and then the NPs are deposited onto carbon support.

A colloidal suspension of Pt NPs ca. 2 nm was synthesized by mixing 4 mL of a solution of NaOH at 0.4 M in EG with 4 mL of a solution of $H_2PtCl_6 \cdot 6H_2O$ at 40 mM in EG in a microwave reaction vessel. The mixture was heated for 3 min at 160 °C with a microwave reactor (CEM Discover SP, 100 W heating power). The solution initially yellow turned dark during the heating.

In order to support the Pt NPs onto a carbon support, 30 mL of 1 M HCl solution was added to 7.3 mL of the colloidal Pt NPs suspension for precipitation. The mixture was centrifuged at 2400 relative centrifugal force (4000 rotations per minute (rpm), Sigma 2–5) for 5 min and the supernatant solvent discarded. This washing/centrifugation with 1 M HCl was repeated twice. Then the Pt NPs were re-dispersed in 7 mL of acetone, and 27.5 mg of carbon black (Vulcan XC72R or Ketjen EC-300J) was added to the suspension. By sonicating the mixture in an ultrasonic bath (Ultrasonic cleaner, VWR) for 1 h, the acetone was evaporated and a dried powder of Pt NPs supported on carbon (Pt/C) was obtained. The dried powder was re-dispersed into water and sonicated for 10 min. The Pt/C catalyst powder was filtered and washed with 200 mL of DI water, and then dried at 100 °C in air.

2.3. Characterization of homemade Pt/C catalysts

The particle size distribution of the Pt NPs obtained from the colloidal synthesis was determined by small-angle X-ray scattering (SAXS) measurements as previously reported [21,22] with a SAXSLab instrument installed at the Niels Bohr Institute of the University of Copenhagen. The particle size distribution of Pt NPs immobilized on the carbon support was determined by transmission electron microscopy (TEM, JEM-2100, JEOL, 200 kV). The size analysis was performed by measuring the size of typically 300 NPs by taking images at 3 different magnifications in 5 different areas of the TEM grid. The Pt loading of the catalyst was evaluated by inductively coupled plasma mass spectrometry (ICP-MS) as previously reported [21]. Measurements were performed at the Max Planck Institute for Iron Research (MPIE) in Dusseldorf, Germany. For sample preparation 100 μL of the catalyst ink was digested in 4 mL of aqua regia (mixture of 30% HCl and 65% HNO_3 in a volume ratio of 1:3) for 90 min on a hot plate at ca. 100 °C. The final volume was finally adjusted to 10 mL with DI water. The sample solutions were filtered to remove residual carbon before the measurements. As the synthesis is very reproducible, we refer for the results of this basic characterization to our previous work [21,22], from which it can be seen that the physical properties of our home-made catalyst are indeed very similar to the commercial TKK catalyst used for comparison, see below (size distribution determined by TEM are 1.9 ± 0.6 nm vs 2.2 ± 0.6 nm for home-made and TKK catalyst, respectively).

2.4. Ink formulation for homemade Pt/C catalysts

4.4 mg of homemade 50 wt % Pt/Vulcan or Pt/Ketjen catalyst powder was mixed with 8 mL of IPA:DI water (1:3, v:v) mixed solvent. A small amount of 1 M KOH solution (8–40 μL) was added as needed to adjust the pH of the ink. The glass vial containing the mixture was placed in an ultrasonic bath filled with cold water (<5 °C) and sonicated for 15 min.

2.5. Ink formulation for commercial Pt/C catalyst

5.97 mg of commercial 46.5 wt % Pt/C catalyst (TEC10E50E, TKK) powder was mixed with 10 mL of IPA:DI water (1:3, v:v)