



## A comparison of rotating disc electrode, floating electrode technique and membrane electrode assembly measurements for catalyst testing



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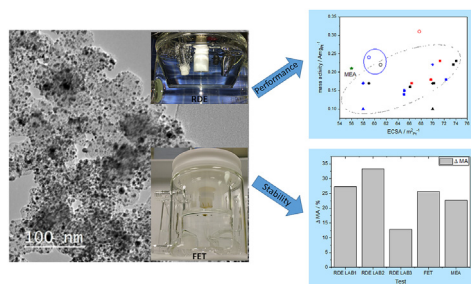
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### HIGHLIGHTS

- Reliable results obtained by new rotating disc electrode catalyst testing protocol.
- RDE data comparable to MEA and floating electrode technique (FET) measurements.
- FET unifies advantages of RDE and MEA.
- FET permits measurements with low amounts of catalyst at high currents.
- New degradation testing protocol results in similar changes in RDE, FET and MEA.

### GRAPHICAL ABSTRACT



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### ABSTRACT

The development of new catalysts for low temperature fuel cells requires accurate characterization techniques to evaluate their performance. As initially only small amounts of catalyst are available, preliminary screening must rely on suitable test methods. In this work, using a carbon supported platinum benchmark catalyst, the rotating disc electrode (RDE) technique was revisited in order to develop a detailed testing protocol leading to comparable results between different laboratories. The RDE results were validated by comparison with data measured both in proton exchange membrane single cells and via the relatively new floating electrode technique. This method can be operated with small amounts of catalyst but does not suffer from low limiting currents and allows prediction of high current capability of newly developed catalysts. Different durability testing protocols were tested with all three methods. Such protocols need to be able to introduce changes in the reference catalyst, but must not be too harsh as otherwise they cannot be applied to alloy catalysts. In all protocols an upper

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potential limit of 0.925 V was used, as this produced degradation in the chosen benchmark catalyst, but still represents realistic conditions for alloy catalysts.

## 1. Introduction

The transportation sector caused nearly 20.5% of total CO<sub>2</sub> emissions in 2014 [1]. This is one reason for the increased interest in electrically driven vehicles (EVs) [2]. The batteries used in battery EVs suffer from low energy density, limited driving range and long charging times [2,3]. Fuel cells (FCs) provide a large driving range of ~500 km, but suffer from high cost due to high Pt content and limited lifetime [4]. Currently, both cathode and anode sides of FCs contain Pt-based catalysts supported on carbon (Pt/C) [5]. While the kinetics of the hydrogen oxidation reaction (HOR) at the anode is very fast, the oxygen reduction reaction (ORR) at the cathode side has a sluggish kinetics, causing voltage losses of hundreds of millivolts [6–8]. Furthermore, Pt catalysts can suffer from poisoning by impurities in fuels, dissolution and agglomeration of Pt particles [9–11]. Costs of the FCs can be reduced by using Pt alloys with increased ORR activity or by complete replacement of Pt [12–14].

Developing new cathode catalysts requires reliable methods to evaluate activity and stability. The data most representative for actual FC performance are obtained by measurements on membrane electrode assemblies (MEA). However, MEA fabrication and characterization are time-consuming, require specific instrumentation, accurate control of gas pressures, temperatures and relative humidities, and large amounts of catalyst material. Newly synthesized catalysts are prepared first in small amounts [15]. Therefore, half-cell tests in aqueous perchloric acid electrolytes (HClO<sub>4</sub>) are preferred for initial screening, typically based on hydrodynamic techniques like the channel flow dual electrode [16] and rotating disc electrode techniques (RDE) [17,18], accelerating oxygen access to the surface and assuring constant limiting currents at large overpotentials. For RDE, a catalyst layer is deposited onto the surface of a glassy carbon (GC) electrode embedded in the RDE holder [19–21]. The large current densities common in FC operation cannot be reached because oxygen solubility in HClO<sub>4</sub> is low, and limiting currents are small, ~6 mA cm<sup>-2</sup> at a rotation rate of 1600 rpm. The technique therefore aims at determining the kinetic current at 0.9 V vs. reversible hydrogen electrode (RHE), calculated from the measured current after applying corrections for ohmic potential drop (iR), capacitive background currents, and mass transport (Koutecký-Levich equation) [22,23]. This current is normalized to the total true electrochemical catalyst surface area (ECSA), determined electrochemically (surface specific activity (SA)) or to the total Pt mass on the electrode (mass activity (MA)).

Because of the wide spread of published values for SA and MA even for identical catalysts, several recent papers have revisited the RDE testing procedure. Garsany et al. recommended procedures resulting in reliable ORR benchmarking results [24], and a method for reproducibly producing smooth electrocatalyst thin films [25] by drop-casting the ink followed by rotational drying at 700 rpm. Uniform catalyst layers with negligible difference in ECSA, but exhibiting higher and more reproducible MA were obtained. Shinozaki et al. [15] found highest activities when omitting Nafion from the ink, but adding a non-ionic surfactant, and evaporating the solvent slowly at 40 °C. The use of a freshly prepared RHE reference electrode (RE) and ultrapure chemicals is recommended [26]. HClO<sub>4</sub> is the recommended electrolyte due to weak ClO<sub>4</sub><sup>-</sup> adsorption, with the concentration determined by a compromise between conductivity and a low impurity level [27]. The determination of the ECSA by hydrogen underpotential deposition (H<sub>UPD</sub>) results in lower values than by carbon monoxide (CO) stripping [28], explained by a potential-dependent contribution of the support capacitance.

ORR activity is usually measured by linear sweep voltammetry (LSV) from more negative to more positive potentials in order to start with an oxide free Pt surface. Scan rates ≤20 mV s<sup>-1</sup> were recommended to minimise capacitive currents [19,29]. At 5 mV s<sup>-1</sup>, lower activities were observed, explained by a larger amount of OH<sub>ads</sub> on the surface and stronger impurity adsorption [19,24,29].

In the new floating electrode technique (FET) developed by Zalitis et al. [30] the ink is applied onto a porous Au coated polycarbonate membrane floating on the electrolyte. Oxygen can reach the catalyst directly through the membrane pores from the gas phase, enhancing mass transport by several orders of magnitude compared to RDE. MA at 0.9 V can be determined without mass transport correction.

The present study is based on the benchmarking of a Pt/C catalyst at four research sites (Lab1–Lab4) with RDE, FET and MEA measurements. After applying current recommendations and protocols, discrepancy was found between the RDE results at Lab1 - Lab3 leading us to further elaborate the procedures and to compare the SA, MA and ECSA obtained with those derived from FET and MEA results (Lab4). Even though no full quantitative agreement can be expected, the general trends in activity and durability must be reflected correctly and be representative for the behavior in an MEA. The results must not depend on the laboratory where they are obtained. Protocols need to be universal enough to be applicable to alloys and pure Pt/C. For this work, a Pt/C catalyst from JMFC was selected as benchmark catalyst. Based on prior experience and the literature, experiments were carried out to optimize certain experimental parameters. Thereby a detailed RDE measurement protocol was established and applied, leading to results reproducible and comparable between groups, and in reasonable agreement with FET and MEA experiments.

## 2. Experimental

### 2.1. Catalysts, chemicals and gases

The 50 wt% Pt/C catalyst (JMFC) was characterized by transmission electron microscopy (TEM) and energy dispersive X-ray spectroscopy (EDS). Isopropanol (IP, Sigma Aldrich, anhydrous 99.5%), 5 wt% Nafion (Sigma Aldrich, Nafion 1100 EW) and 18.2 MΩ cm<sup>-1</sup> water were used to freshly prepare a catalyst ink (concentration: 0.2 mg<sub>Pt</sub> ml<sup>-1</sup>) by adding 4 mg of 50 wt% Pt/C catalyst to a mixture of 7.96 ml water, 2 ml IP and 40 μl 5 wt% Nafion solution and ultrasonating it for 15 min to disperse the catalyst homogeneously. Prior to use, it was sonicated for additional 40 s. For the sonication a Bandelin Sonopulse HD 3200, a Branson Sonifier 150 or a Branson Digital Sonifier 450, all with a 3 mm outer diameter horn tip were used at the lowest possible intensity. To limit ink warming, the container was placed in a water or ice bath during sonication. 10–30 μl ink were applied to the electrode (catalyst loading of 10–30 μg<sub>Pt</sub> cm<sup>-2</sup>). Electrochemical measurements were carried out in freshly prepared 0.1M HClO<sub>4</sub> (from concentrated HClO<sub>4</sub>, Acros Organics, p.A., Fluka TRACeselect, Ultrex II Ultrapure Reagent (JT Baker) or Sigma Aldrich). Gases for purging of cells and electrolyte were Ar (5.0, Westfalengas), N<sub>2</sub> (Air Liquide Ultrapure) and O<sub>2</sub> (5.0, Westfalengas or Air Liquide Ultrapure).

### 2.2. Electrode preparation

The GC electrode (ø 5 mm) was polished to a mirror finish using 1 μm alumina-particle suspension (MicroPolish™Buehler) on a moistened polishing microcloth (Buehler MicroCloth PSA) and then 0.05 μm alumina-particle suspension (MicroPolish™Buehler) on a nylon

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