



# High temperature stability study of carbon supported high surface area catalysts—Expanding the boundaries of ex-situ diagnostics



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## ARTICLE INFO

### Article history:

Received 21 April 2016

Received in revised form 15 June 2016

Accepted 20 June 2016

Available online 21 June 2016

### Keywords:

PEM fuel cells

Electrocatalyst stability

Ex-situ diagnostics

High temperature

Stability enhancement

## ABSTRACT

The performance of proton-exchange membrane fuel cells (PEMFCs) is defined by the equally important parameters of the intrinsic activity and stability of the electrocatalysts. This work focuses on the stability of carbon supported high surface area oxygen reduction reaction catalysts at potentials and temperatures similar to the operating conditions of PEMFCs. The catalysts used for this investigation consist of Pt nanoparticles of the same particle size supported on two types of carbon support having different textural properties, i.e., Vulcan and Hollow Graphitic Spheres (HGS). A broad toolbox of characterization techniques is utilized at 60 °C in order to resolve the contribution of the different degradation mechanisms, namely nanoparticle coalescence, metal dissolution and the corrosion of carbon support, to the total active surface area loss. The results obtained by investigating the impact of temperature, potential treatment and catalyst layer morphology on the aging behavior lead to a deeper understanding of the aging mechanisms and their interrelation at application-relevant conditions. Moreover, the previously reported improved performance of the Pt/HGS catalyst is confirmed also under higher temperatures. The experimental approach introduced in this work, highlights new challenges for high-temperature degradation investigations with supported PEMFC catalyst.

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## 1. Introduction

In recent decades the gradual phasing out of conventional power sources in favor of renewables has raised the interest in the development of efficient energy conversion and storage strategies, including the further improvement of electrochemical devices such as fuel cells and electrolyzers [1,2]. Proton-exchange membrane fuel cells (PEMFCs) are mainly intended for application in the automobile section. However, in order to be a feasible alternative to combustion engines they have to satisfy strict performance and cost criteria [3,4]. Among other factors, the latter hinge strongly on the performance of the electrocatalyst in terms of intrinsic activity, i.e. the provided current per surface area or per

mass of the electrocatalyst, and in terms of stability, i.e. the durability of the catalyst within the operating conditions of the electrochemical reactor.

The oxygen reduction reaction (ORR), occurring on the cathode of a PEMFC, is a complex multi-stepped reaction, which has been the focus of intensive research due to its high potential for optimization. Even on carbon-supported Pt-based catalysts, which are among the most active materials for the reaction, the kinetic losses are still in the range of hundreds of mV in operation. Moreover, the harsh conditions with respect to temperature and positive potentials during the ORR can lead to severe degradation of the active material. Despite being considered as sufficiently stable, Pt-based materials can also significantly deteriorate during operation. The degradation is thereby linked to a variety of complex phenomena on the nanoscale material level [5,6], but also on the mesoscale level of the electrode structure [7,8].

The instability of the electrocatalyst results in the loss of the active electrochemical surface area (ECSA) and overall performance, two macroscopic parameters that can be used as

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quantitative descriptors for the extent of degradation. However, they cannot provide any information on the exact mechanism, which would be important for the development of mitigation strategies. Namely, as it was shown recently [9], there is a complex interaction between precisely defined degradation mechanisms that can contribute to the performance loss. These mechanisms can be separated into: (i) processes that interest solely the degradation of the Pt catalyst, which include Pt dissolution [10–13] and Pt nanoparticle growth as a result of agglomeration and/or coalescence [14,15]; (ii) processes related to the degradation of the carbon support, [16–21] taking place predominantly at the support-nanoparticles interface, which result in nanoparticle detachment [22] or nanoparticle growth because of the shrinkage of the support [14]; (iii) indirect mechanisms like Ostwald ripening [5,6,23], which entails the dissolution of Pt species and its redeposition on neighboring nanoparticles (resulting in particle growth) or on the support.

Various studies have already investigated the aforementioned mechanisms either in-situ, that is, directly in fuel cells [5,24], or via ex-situ approaches, mostly based on liquid- electrolyte-type cells. The first type of investigations, despite the apparent advantages, is time consuming and usually it lacks in providing fundamental information about solely the behavior of the electrocatalyst, as its degradation is often masked by the intricacy of the electrode structure and by the complexity of the analytical system. On the other hand, the ex-situ characterizations often tend to neglect or/and underestimate crucial parameters, such as the influence of the temperature [25–27]. Specific ex-situ characterization attempts have been also reported which are focusing on electrocatalytic performance investigations under more application relevant conditions of temperature or pressure [28–31]. Nevertheless, these research efforts, although insightful, aimed in investigating in separate the aforementioned aging factors. Consequently, the understanding of the complex interplay between the different degradation mechanisms at elevated temperatures is still vague.

In this work we utilize a broad toolbox of advanced of characterization techniques – all employed at high temperatures – to analyze separately all the possible origins of ECSA losses and to rationally disentangle them. For this purpose, two HSACs, which were previously investigated at room temperature [32], are examined. The goal is to extend these investigations at higher temperature. Furthermore, this work intends to introduce, through the analysis of these case studies, a general electrocatalytic characterization approach for high temperature studies, extending the existing boundaries of ex-situ characterization stability measurements. The experimental methodologies employed in this study are based on: (i) the rotating disk electrode (RDE) setup for standard electrochemical characterizations, (ii) identical location transmission electron microscopy (IL-TEM) to visualize the degradation of the electrocatalyst on the nanometer scale at identical locations and at consecutive stages of the stability tests [22]; (iii) a scanning flow cell (SFC) coupled to inductively-coupled-plasma mass-spectrometry (ICP-MS) to investigate Pt dissolution [33]; (iv) a SFC coupled to an online electrochemical mass spectrometer (OLEMS) [34] to study the corrosion of the carbon support. This experimental approach aims at highlighting the dominating stability issues of HSACs under application-relevant temperatures. Concurrently, a catalytic design which could circumvent the prevailing catalytic aging limitations is proposed.

## 2. Experimental

### 2.1. High surface area catalysts

Two different types of high surface area Pt-based electrocatalysts are compared in this study. Both catalysts consist of Pt

nanoparticles with a particle size diameter of around 3–4 nm and a metal loading of 20 wt.%. The main difference between the two samples, i.e. Pt/Vulcan and Pt/HGS, hinges on the specific support utilized. While the former refers to Vulcan XC72 R with a BET of ca.  $250 \text{ m}^2 \text{ g}^{-1}$ , the latter is a partially graphitized mesoporous carbon framework with a BET of ca.  $1200 \text{ m}^2 \text{ g}^{-1}$  in the shape of hollow spheres (hereafter, named as Hollow Graphitic Spheres, i.e. HGS [35]). The synthesis procedures for both catalysts and particularly the encapsulation of Pt nanoparticles in the interconnected pores of the HGS network have been described in detail in our previous work [32].

### 2.2. Electrochemical characterization

#### 2.2.1. Cell

The electrochemical characterization was performed in an RDE setup. The RDE tip (5 mm in diameter,  $0.196 \text{ cm}^2$  of geometrical surface area) is made of glassy carbon and it is embedded in a Teflon shaft. The electrochemical measurements were carried out in a Teflon three- compartment cell. A graphite rod was used as counter electrode and a saturated Ag/AgCl electrode (Metrohm) as reference electrode. The reference electrode was further separated from the main compartment with a Nafion membrane to avoid chloride contamination during the extensive degradation measurements. The electrolyte employed throughout the study was 0.1 M  $\text{HClO}_4$  prepared with ultrapure water (18 M $\Omega$ , Millipore) and concentrated  $\text{HClO}_4$  (Merck, Suprapur). In all measurements positive feedback was applied for the compensation of the electrolyte resistance so that the residual uncompensated resistance was  $< 2 \Omega$  in all experiments [36]. Temperature control was achieved by means of a thermostatic bath/circulator (Lauda).

#### 2.2.2. Catalyst Suspension, deposition and loading

For both electrocatalysts, the catalytic powder was weighed on a high-precision microbalance and then suspended in 5 mL of ultrapure water to prepare the so-called catalyst “ink”. In order to achieve a homogeneous dispersion, the suspensions were usually sonicated for approx. 30 min and 45 min for Pt/Vulcan and Pt/HGS, respectively. A 20  $\mu\text{L}$  aliquot of the ink was deposited on the RDE tip to create the catalyst film. The drying step was carried out in air and the metal loading for all RDE experiments corresponded to  $20 \mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ . 7  $\mu\text{L}$  of 1:50 Nafion:isopropanol solution was added on top of the thin catalytic film in order to prevent the detachment of the catalyst from the glassy carbon during the accelerated aging test.

#### 2.2.3. Degradation protocol

The applied degradation protocol comprised a series of 10000 potential cycles (triangular wave) at  $60^\circ\text{C}$  with a scan rate of  $1 \text{ V s}^{-1}$  in the potential range of 0.4 to  $1.0 \text{ V}_{\text{RHE}}$  and 0.4 to  $1.2 \text{ V}_{\text{RHE}}$ . The tests were carried out in argon saturated electrolyte and without rotation. All potentials are given with respect to the reversible hydrogen electrode (RHE) potential, which was determined for each experiment separately and with an accuracy of 1 mV. The active surface area was monitored throughout the degradation tests by means of CO-stripping.

Our previous investigations have shown that the surface of the ‘as-received’ Pt/HGS catalyst is blocked by impurities and/or carbonaceous residues originating from the synthesis process, which can hinder the accessibility of the Pt active sites [32,37,38]. For this reason Pt/HGS was always electrochemically activated prior to the measurement with 360 potential cycles at room temperature ( $0.4 \text{ V}_{\text{RHE}}$  to  $1.4 \text{ V}_{\text{RHE}}$ ,  $1 \text{ V s}^{-1}$ ). An equivalent cleaning treatment (20 potential cycles) was applied to the Pt/Vulcan catalyst.

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