



Comparative degradation study of carbon supported proton exchange membrane fuel cell electrocatalysts – The influence of the platinum to carbon ratio on the degradation rate



Jozsef Speder^{a,*}, Alessandro Zana^a, Ioannis Spanos^a, Jacob J.K. Kirkensgaard^b, Kell Mortensen^b, Marianne Hanzlik^c, Matthias Arenz^{a,*}

^aNano-Science Center, Department of Chemistry, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

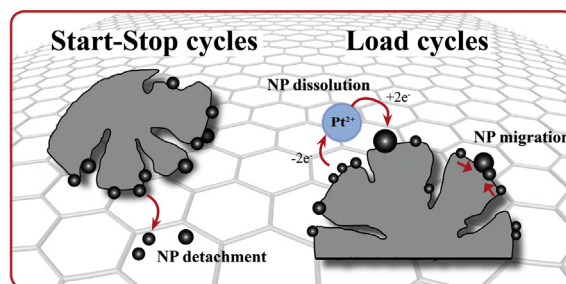
^bNiels Bohr Institute, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

^cTechnical University of Munich, Zentrum Elektronenmikroskopie, D-85747 Garching, Germany

HIGHLIGHTS

- Study of influence of Pt:C ratio on the degradation behaviour of Pt/C catalysts.
- Pt:C ratio influences degradation under start-up/shutdown conditions.
- Pt:C ratio has small influence on degradation under load cycles.
- Degradation on Vulcan XC72R substantial higher than on Ketjenblack EC-300.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 7 January 2014

Received in revised form

4 March 2014

Accepted 10 March 2014

Available online 20 March 2014

Keywords:

Colloidal toolbox synthesis

Proton exchange membrane fuel cells

Electrocatalyst durability

Degradation mechanisms

Carbon corrosion

ABSTRACT

A colloidal synthesis approach is used to prepare supported proton exchange membrane fuel cell (PEMFC) catalysts with various Pt loadings – from low to extremely high ones. The catalyst samples are used to continue our investigation of the role of the Pt:C ratio in the degradation processes. The influence of the platinum loading on the electrochemical surface area (ECSA) loss is evaluated in a systematic electrochemical study by using two commercially available carbon blacks, namely Vulcan XC72R and Ketjenblack EC-300J. Accelerated degradation tests simulating load cycle and start-up/shutdown conditions are carried out in accordance with the Fuel Cell Commercialization Conference of Japan (FCCJ) recommendations. Under conditions simulating the load cycle of PEM fuel cells no unambiguous correlation between the ECSA loss and the Pt:C ratio is found. By contrast, under conditions simulating the repetitive start-up/shutdown processes of PEMFCs the ECSA loss first increases with increasing Pt loading. However, it decreases again for very high loadings. Furthermore, the Vulcan samples exhibited higher ECSA losses than the Ketjenblack samples, indicating the important role of the physical and chemical properties of pristine carbon supports in the carbon degradation mechanism.

© 2014 Elsevier B.V. All rights reserved.

* Corresponding authors. Tel.: +45 35320002; fax: +45 35320214.

E-mail addresses: spederj@gmail.com (J. Speder), m.arenz@chem.ku.dk (M. Arenz).

1. Introduction

A significant challenge for the commercial viability of proton exchange membrane fuel cells (PEMFCs) is the activity and stability [1–5] of the catalysts used for promoting the electrochemical energy conversion reactions. In the last years our research group

focused on investigating the stability of catalysts. The chosen strategy was to apply measurements in electrochemical half-cells in order to enable fast and systematic assessments and to exclude the influence of “design” factors, for example the specific composition and preparation of the catalyst coated membrane (CCM). We introduced a specific investigation tool, dubbed identical location – transmission electron microscopy (IL-TEM), allowing for the first time at the nanoscale a direct comparison of same catalyst areas before and after treatment [6]. It could for example be shown that a specific commercial catalyst under the applied treatment conditions almost exclusively degraded via a particle detachment process [6,7]. In further studies of our and other groups the influence of parameters such as the carbon support or the Pt to carbon ratio on the stability of catalysts was investigated [8–12]. Comparing the degradation of different commercial catalysts, however, faced two drawbacks that inhibited truly systematic measurements. First, the absolute control over the synthesis, i.e. the ability to vary individual catalyst parameters (for example the Pt loading) while leaving others constant (for example the particle size and chemical state of the carbon support), was not given for commercial catalysts [12,13]. Additionally, the exact synthesis protocol of such samples is either not known or it is confidential. This drawback was mainly resolved by adapting a colloidal synthesis approach for the synthesis of the PEMFC catalysts [14]. The developed tool-box approach enables exactly this, selectively changing parameters like the Pt loading or the type of support material [15].

Second, a more systematic degradation treatment, i.e. standardized accelerated stress test (AST) conditions that are feasible for half-cell measurements (degradation treatments lasting several days are hardly feasible for half-cells) were needed. Such an AST treatment was recently proposed by the Fuel Cell Commercialization Conference of Japan (FCCJ) [16]. Two separate treatment conditions are recommended. One treatment simulates load cycle conditions, the second start-up/shutdown (Start–Stop) conditions of a PEMFC, thus enabling to investigate how specific operation conditions affect the degradation.

With both tools now at hand, truly systematic investigations of the degradation process of PEMFC catalysts are feasible, which hopefully amends a “material by design” approach for their development. In the presented study, we are focussing on the influence of the ratio between Pt and carbon on the degradation. In our recent work, we found that the measured electrochemical surface area (ECSA) loss in AST treatments strongly depends on the treatment conditions, i.e. treatments simulating load cycles and start-up/shutdown conditions [17]. These initial results are further investigated and complemented by careful microscopic (IL-TEM) as well as spectroscopic (small angle X-ray scattering; SAXS) investigations. Furthermore, the range of different Pt loadings (Pt to C ratios) was considerably extended revealing unexpected trends.

2. Experimental

2.1. Catalyst preparation

The investigated catalysts, hereafter called Pt/C, were synthesized in-house as described by Speder et al. [15]. The synthesis consists of two steps. First, a solution of colloidal Pt NPs with narrow size distribution of around 2 nm is prepared, then the NPs are deposited in varying amounts onto the high surface area (HSA) carbon support, i.e. Ketjenblack EC-300J (AkzoNobel, Brunauer–Emmett–Teller (BET) total surface area: $776 \text{ m}^2 \text{ g}^{-1}$, thereof $416 \text{ m}^2 \text{ g}^{-1}$ external (pores $> 2 \text{ nm}$) and $360 \text{ m}^2 \text{ g}^{-1}$ internal (pores $< 2 \text{ nm}$)), or Vulcan XC72R (Cabot Corporation, total BET area: $222 \text{ m}^2 \text{ g}^{-1}$, thereof $154 \text{ m}^2 \text{ g}^{-1}$ external and $68 \text{ m}^2 \text{ g}^{-1}$ internal [18]). Catalysts samples were prepared between 10 and

80 wt. % Pt. For a more detailed description of the Pt NP preparation the reader is referred to Refs. [14,15]. Briefly, a colloidal suspension of Pt NPs is synthesized by mixing under vigorous stirring 50 ml of a 0.4 M NaOH/ethylene glycol solution with a solution of 1.0 g $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ dissolved in 50 ml ethylene glycol, in order to obtain a yellowish platinum hydroxide or oxide colloidal solution. The colloidal solution is then heated to $160 \text{ }^\circ\text{C}$ for 3 h to obtain a blackish-brown homogeneous metal particle colloidal suspension. The size and structure of the thus synthesized Pt NPs are controlled by transmission electron microscopy (TEM). The average diameter of the obtained Pt NPs is typically around 2 nm exhibiting a narrow size distribution. In order to support the Pt NPs onto an HSA carbon first 40 ml of HCl was added to the colloidal NP solution for precipitation. The solution was centrifuged (4000 rpm, 6 min) and repeatedly washed with 1 M HCl before dispersing it in acetone. The as-synthesized Pt NPs were deposited onto different HSA carbons by mixing the NP suspension with carbon black in 3 ml of acetone and sonicating for 1 h. Finally the catalyst was dried.

The Pt loading of the catalysts was confirmed by using inductively coupled plasma mass spectrometry (ICP-MS) measurements. For this, the catalysts were dissolved in inverse aqua regia (freshly mixed cc. HNO_3 and cc. HCl in a volumetric ratio of 3:1, respectively). The concentration of platinum in the diluted aqua regia solution was analyzed by ICP-MS (NexION 300X, Perkin Elmer) through a Meinhard quartz nebulizer and a cyclonic spray chamber, operating at nebulizer gas flow rates of between 1.0 and 1.02 L min^{-1} (Ar, purity 5.0).

2.2. Electrochemical characterization

The electrochemical measurements were performed in an all-Teflon three-compartment electrochemical cell [19], using a home-built multi-electrode setup with eight glassy carbon (GC) tips used as working electrodes (WE). The potential was controlled using a potentiostat (Princeton Applied Research, model 263A) in a three electrode setup. The counter (auxiliary) electrode was a carbon rod, the reference electrode a Schott Ag/AgCl/KCl(sat.) electrode located in a second compartment separated by a membrane (Nafion®) in order to avoid the diffusion of Cl^- ions into the main compartment [20]. All potentials, however, are referred to the reversible hydrogen electrode (RHE) potential, which was experimentally determined for each measurement series. All acid solutions were prepared from Millipore® water ($>18.3 \text{ M}\Omega \text{ cm}$, Total Oxidizable Carbon, TOC $< 5 \text{ ppb}$) and Suprapur acids (Merck). The measurements were performed at room temperature. Prior to the RDE measurements the glassy carbon (GC) working electrode (5 mm diameter, 0.196 cm^2 geometrical surface area) was polished to mirror finish using alumina oxide paste, 0.3 and $0.05 \text{ }\mu\text{m}$ (Buehler-Met, de-agglomerated α -alumina and γ -alumina, respectively), and cleaned ultrasonically in ultrapure water and cc. 70% HClO_4 . The catalyst ink was prepared by mixing the catalyst powder with ultrapure water to a concentration of $0.14 \text{ mg}_{\text{Pt}} \text{ cm}^{-3}$ and ultrasonically dispersing the suspension for 30 min. Before applying the catalyst ink to the GC electrode the suspension was ultrasonically dispersed for an additional 5 min. Then a volume of $20 \text{ }\mu\text{L}$ of the suspension was pipetted onto the GC electrode leading to a Pt loading of $14 \text{ }\mu\text{g}_{\text{Pt}} \text{ cm}^{-2}$ and thereafter dried in a nitrogen gas stream. Care should be taken that the catalyst ink is not heated from the ultrasonic bath, to avoid errors from changing water density. All electrochemical experiments were performed in 0.1 M HClO_4 solution. Prior to the measurements the electrolyte was de-aerated by purging with Ar gas (99.998%, Air Liquide), and the measurements were started with cleaning the catalyst by potential cycles between 0.05 and $1.0 \text{ V}_{\text{RHE}}$ at a scan rate of 50 mV s^{-1} . For the measurement of the RHE the electrolyte (0.1 M HClO_4) was purged with hydrogen

Download English Version:

<https://daneshyari.com/en/article/7736332>

Download Persian Version:

<https://daneshyari.com/article/7736332>

[Daneshyari.com](https://daneshyari.com)