



The colloidal tool-box approach for fuel cell catalysts: utilizing graphitized carbon supports



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ABSTRACT

In the presented study we apply the “tool-box” approach for studying colloidal Pt nanoclusters as building blocks for polymer electrolyte membrane fuel cells (PEMFCs) catalysts utilizing graphitized carbon as support. In line with previous studies we concentrate on the influence of the carbon support on the degradation of PEMFC catalysts. It is demonstrated that a mild etching of the graphitized carbon support can lead to an improved stability under accelerated stress tests targeting carbon corrosion.

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1. Introduction

Colloidal metal nanoclusters stabilized by simple ions are promising building blocks for supported catalysts [1,2]. In recent years we deployed colloidal nanoclusters for the systematic investigation of Pt based catalysts for polymer electrolyte membrane fuel cells (PEMFCs) and coined the term “tool-box” synthesis [3–8]. The basic concept of the tool-box synthesis is the ability to systematically change individual parameters of the catalyst, while the other parameters remain constant. The synthesis basically consists of two steps. First a colloidal “mother” suspension of Pt or Pt-alloy nanoparticles (NPs) is prepared. The NPs are stabilized by simple, non-strongly binding ions [1,9], which can easily be removed without changing the NPs, i.e. without the typical applied heating steps, ozone treatment etc. [10–16]. Then in the second step, the NPs are attached to a high surface area support by a simple drying procedure, which does not affect the NP or the support properties. Thus the synthesis allows us for example to change the Pt loading on a carbon support at constant, well-defined particle size [3,5], or to obtain a constant loading on different carbon supports [7]. Even though the obtained catalysts perform comparable to industrial samples, the main purpose of such studies is to bridge the gap between basic and applied research. That is to perform “use inspired basic research”.

In the last decade most research concerning fuel cell catalysts was focused on the development of new, highly active catalytic materials [17]. In light of the obtained improvements—especially in the field of non-precious metal catalysts [18], “plain” activity optimization may no longer be the most important goal [19]. Instead the aim needs to be to concurrently increase durability and power density (for a given amount of Pt). In our research group, in recent years we therefore focused on fuel cell catalyst stability. One of the main limitations concerning the stability of conventional high surface area (HSA) Pt/C catalysts is the stability of Pt NPs as well as the corrosion of the carbon support [20–26]. Efforts to exchange the carbon support by more stable, oxide based supports may exhibit some improvements in half-cell tests [27], but the excellent properties of carbon (for example its porosity) are more decisive for the performance in membrane electrode assemblies or fuel cell stacks.

The presented work therefore focuses on the characterization of catalysts supported on graphitized carbon blacks (GCB). The improved corrosion resistance of GCBs as compared to standard CBs (i.e. Vulcan XC72R) is long known and makes them an interesting support for Pt NPs [28]. However, due to the less defective nature of GCBs the challenge is to reach a high dispersion of Pt during the synthesis of Pt/GCB. In conventional synthesis, due to the small amount of agglomeration sites, the formation of large particles is favored. On the other hand, creating surface sites by etching of the carbon poses the risk of destroying the carbon structure and inducing surface sites for carbon corrosion. Here we investigate a possible strategy to circumvent these difficulties. Applying our “tool-box” synthesis approach we investigate GCBs

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that has been mildly etched before particle attachment. The goal is to generate just the right amount of anchoring sites for Pt NPs, but without destroying the ordered carbon structure.

2. Experimental

2.1. Colloidal synthesis approach of carbon supported Pt nanoparticles

The catalysts used in this work were in house synthesized based on the original recipe of colloidal Pt nanoclusters by Wang et al. [9] as described in our previous work [4]. As mentioned above, first a colloidal “mother” suspension of Pt NPs with a narrow size distribution and an average particle size of about 2 nm was synthesized via an ethylene glycol route (EG). Then, in the second step, different catalysts were made from the same mother solution by washing, re-dispersing and drying Pt NPs onto various carbon supports. As carbon supports Vulcan XC72R (Cabot Corporation, in the following named Vulcan), GCB and GCB treated in H_2O_2 (GCB H_2O_2) were used. The GCB support was provided by Umicore AG & Co KG. It was obtained by graphitizing Ketjenblack EC-600JD carbon support (Akzo Nobel) in an inert atmosphere at 3200 °C.

In the following the individual steps of the catalyst synthesis are shortly described. For a more detailed description of the EG synthesis and the so called “tool box” approach see Refs. [4,9]. The colloidal solution containing Pt NPs was synthesized by mixing a solution of ethylene glycol and NaOH with an ethylene glycol (EG) solution of $H_2PtCl_6 \cdot H_2O$ in EG. A typical recipe, the one used here, is to use 50 mL of 0.4 M in NaOH-EG mixed with 1.0 g $H_2PtCl_6 \cdot H_2O$ precursor dissolved in 50 mL EG. Alternatively also smaller amounts can be prepared when keeping the concentrations and ratios constant. The yellowish platinum hydroxide or oxide colloidal solution in EG was subsequently heated to 160 °C for 3 h under reflux in an Ar atmosphere. During heating a blackish-brown homogeneous metal particle colloidal suspension with a Pt concentration of 4 g_{Pt}/l_{EG} forms. Alternative to an oil heating bath, a microwave reactor can be applied [29], which renders the particle synthesis extremely fast. The obtained particle suspension is stabilized by the adsorption of simple ions and can be used as mother suspension for different catalysts with identical Pt NPs. The size of the thus synthesized Pt NPs in EG can be checked by small angle X-ray scattering (SAXS) and is very reproducible around 2 nm in diameter exhibiting a narrow size distribution.

To support the Pt NPs onto the carbon powder 1 M HCl was added to the colloidal NP solution in a ratio of ca. 2:1 (ml/ml; HCl/NP solution) for precipitation. The solution was centrifuged (4000 rpm, 6 min) and the supernatant solvent discarded. This

procedure was repeated before re-dispersing the NPs in acetone. Finally, the as-synthesized Pt NPs were deposited onto the different carbon supports by mixing the NPs suspension (in acetone) with carbon mixed in 3 mL of acetone and sonicating for 1 h. The catalyst samples were prepared with two different nominal Pt loadings; i.e. 30 wt.% Pt/Vulcan as well as 10 wt.% Pt/GCB and 10 wt.% Pt/GCB H_2O_2 . Finally the catalyst is dried. Efforts to increase the Pt loading of the GCB supports without loss in surface area were not successful.

The actual Pt loading of the catalysts was determined by using inductively coupled plasma mass spectrometry (ICP-MS) measurements. For this, the catalysts were dissolved in aqua regia (freshly mixed cc. HNO_3 and cc. HCl in a volumetric ratio of 1:3, 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 15 $L\ min^{-1}$ (Ar, purity 5.0).

2.2. H_2O_2 treatment of graphitized carbon

To enhance particle support interaction, the graphitized carbons treated in H_2O_2 . For this 50 mg of GCB powder was mixed under vigorous stirring into 100 ml of 33% H_2O_2 solution using a closed vial. The suspension was then heated to 100 °C and kept at this same temperature under stirring for 2 days. Then the suspension was cooled down to room temperature and centrifuged at 4000 rpm for 30 min to remove the remaining H_2O_2 . Finally the treated GCB H_2O_2 powder was rinsed twice with MilliQ water and then dried in an oven at 80 °C over night.

2.3. Electrochemical measurements

The electrochemical measurements were performed in a homemade all-Teflon three compartment cell [30,31]. A carbon rod has been used as a counter electrode (CE), a home build multi-electrode with eight glassy carbon tips served as working electrodes (WE). The potential was controlled using a potentiostat (Princeton Applied Research, model 263A) in a three electrode setup. The reference electrode (RE) was a Schott standard calomel electrode (SCE) placed in a compartment separated by a membrane (Nafion[®]) in order to avoid the diffusion of Cl^- ions into the main compartment [32]. All potentials however are referred to the reversible hydrogen electrode (RHE) which was experimentally determined for each measurement series. The electrolyte was prepared using Millipore[®] Milli-Q water ($>18.3\ M\ \Omega\ cm^{-1}$, total

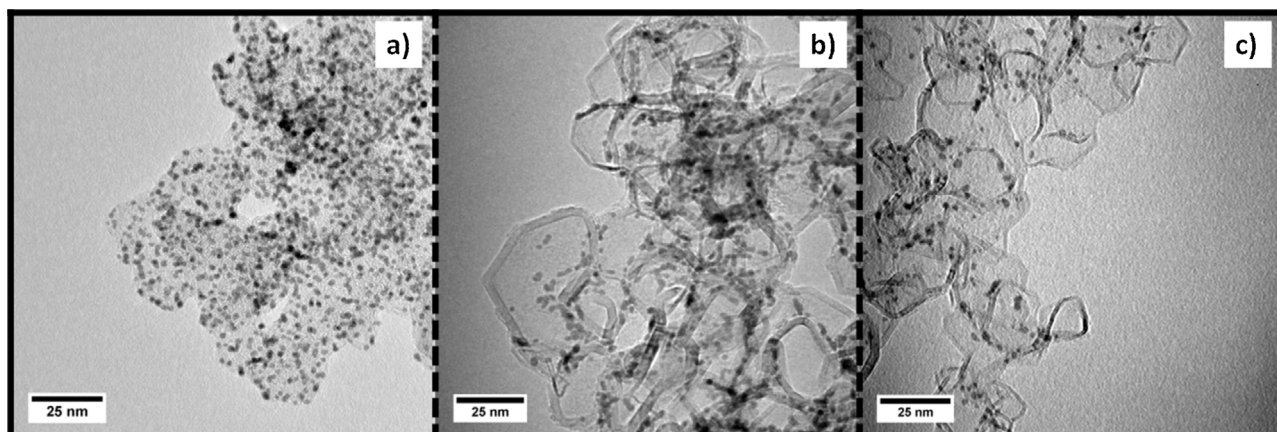


Fig. 1. TEM micrographs of the synthesized Pt/C catalysts. a) 30 wt.% Pt/Vulcan, b) 10 wt.% Pt/GCB, c) 10 wt.% Pt/GCB H_2O_2 .

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