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Streamlining of the synthesis process of Pt/carbon xerogel electrocatalysts with high Pt loading for the oxygen reduction reaction in proton exchange membrane fuel cells applications

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ABSTRACT

Pt/carbon xerogel catalysts were synthesized by different methods. The strong electrostatic adsorption (SEA) method, which consists in enhancing electrostatic interactions between the support and the precursor, was first modified in order to avoid any Pt loss (charge enhanced dry impregnation, CEDI). In a second step, the synthesis was rationalized to speed up the reduction (liquid phase reduction with sodium borohydride, $NaBH_4$). The synthesis procedure was further simplified in order to obtain one-step procedures, such as (i) reduction of highly loaded platinum solution by sodium borohydride, (ii) formic acid reduction, and (iii) colloid synthesis. All the catalysts were analyzed by physicochemical and electrochemical methods. They are compared to a reference commercial catalyst (Tanaka). The best performances are obtained by the SEA, the CEDI and the formic acid reduced catalysts, the performance of which are at least equal to, or even higher (up to 20–25% in mass activity) than those of the commercial reference. From these three methods, the only one-step method is the formic acid reduction, which allows avoiding time-consuming drying and H_2 reduction steps.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are promising and eco-friendly power generators. However, they are not widely commercialized yet. This is especially because of the high cost of the device, which is partly due to one of its major component: the catalytic layer. Indeed, common catalytic layers are constituted of Pt or Pt-based nanoparticles supported on high surface area carbon (Pt/HSAC) [1]. These catalytic layers usually display high Pt loading, which increases the fuel cell price as Pt is an expensive metal with supply limitations [2,3]. One of the fuel cell researchers' main objectives is therefore to decrease the Pt loading of the catalytic layers while keeping high performances.

To do so, the increase of the Pt dispersion on the support was studied in order to increase the number of active sites available for reaction, *i.e.* the number of Pt atoms at the surface of the particles. The number of active sites increases when the Pt particle size decreases, *i.e.* when the Pt specific surface area increases. Indeed, the smaller the Pt particle size, the higher the Pt specific surface area. However, too small Pt nanoparticles lead to a decrease in activity of the surface Pt atoms for most of the reactions performed in PEMFCs, such as the oxygen reduction reaction (ORR). Indeed, these reactions are structure-sensitive [4]. So, the specific activity (*i.e.* current per surface unit of Pt) for the ORR increases with the particle size (up to several tens of nm). Therefore, the optimal Pt nanoparticles size, resulting in best mass activity (*i.e.* current per mass unit of Pt) is around 3–4 nm [5,6].

Over the years, many methods to synthesize Pt/carbon catalysts with high Pt loading and particle size distribution suitable for applications in PEMFCs have been developed [7,8]. Among the most popular ones, one can cite the impregnation of the support using a metal precursor (followed by drying and reduction treatment) and the impregnation-precipitation methods (where the metal precursor is directly reduced to precipitate onto the support), colloidal techniques (where a Pt particle colloid is first formed, then contacted with the support) [9], polyol methods (where a metal precursor is reduced by polyhydroxylic alcohol, often in the presence of a surfactant) [10,11], the deposition of metal clusters from the gas phase (by physical/chemical vapor deposition or by metal sputtering) [12,13] or even plasma-derived techniques (where the Pt precursor is contacted with the support and decomposed by plasma treatment) [14]. Regarding the support, many carbons have been used, from classical carbon blacks to nanostructures like nanotubes or graphene [15,16]. In the last decade, carbon xerogels (CXs), *i.e.* nanostructured carbons prepared by drying and pyrolysis of organic gels, have been used by a few research groups [17–24]. The

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main interest of such supports lies in their better electrode architecture control and enhanced mass transport properties [18]. Recently, in an effort to synthesize Pt/carbon xerogel catalysts with high metal loading and high dispersion, the strong electrostatic adsorption (SEA) method [25–27] was especially developed on such nanostructured carbon supports. The SEA technique consists in maximizing the electrostatic interactions between the metal precursor and the support by adjusting the pH of the carbon/water/Pt precursor slurry to the adequate value. This value depends on the surface chemistry of the support and on the nature of the Pt precursor. Due to the presence of various oxygenated surface groups, the carbon support protonates/deprotonates at low/high pH value. This enhances the adsorption of anions/cations, respectively. For example, in the case of the impregnation of CXs by hexachloroplatinic acid (CPA, H_2PtCl_6) aqueous solutions (1000 ppm_{Pt}), the highest Pt uptake occurs at a final pH around 2.5, which yields a Pt loading ca. 8–10 wt.% [27]. In order to achieve high Pt mass fraction without sacrificing the dispersion, the SEA procedure can be performed several times consecutively with fresh Pt precursor solution [27] or with the same (recycled) Pt precursor solution [22].

However, the size of the Pt particles synthesized by the SEA technique is *ca.* 2 nm [22], which is below the optimal value for PEMFC catalysts [5,6]. Another drawback of this method is the complexity of the procedure to obtain catalysts with high Pt loading. Indeed, in order to synthesize highly loaded Pt/CX catalysts (> 20 wt.%), the CX undergoes several synthesis steps, *i.e.* adsorption of Pt ions, filtration, drying, and reduction under hydrogen, which must be repeated several times since one single cycle leads to 8 wt.% in Pt. All these steps are time-consuming. As an example, three days at least are required to synthesize 20 wt.% Pt/CX *via* SEA (1 day for each impregnation-reduction cycle). This implies that some adaptations/modifications must be performed on the synthesis procedure in order to obtain easy-to-make Pt/CX catalysts with high performances.

The purpose of the first synthesis modification performed in our previous studies so far was to avoid Pt loss. To do so, the charge enhanced dry impregnation (CEDI) method was used [28]. It combines the advantages of (i) the SEA method, as the pH of the Pt precursor solution is fixed at an optimal value in order to maximize the interactions between the metallic ions and the support, which leads to a high metal dispersion, and (ii) the dry impregnation (DI) method, as the volume of the precursor solution strictly corresponds to that necessary to fill the pores of the support. This strategy avoids Pt loss during the synthesis. Cao et al. [28] synthesized Pt/CX catalysts with 10 wt.% Pt loading in one impregnation-reduction cycle with CPA as precursor.

Another modification of the synthesis was investigated in previous works: one-step deposition methods. These allow to deposit large Pt quantity on CX in one single impregnation-reduction step. One-step syntheses lead to highly loaded Pt/CX catalysts synthesized within a few hours, whatever the final loading.

One of these one-step syntheses, developed by Alegre et al. [29], uses sodium borohydride (SB) as a reductant. It consists in the impregnation of the CX support, followed by reduction with SB, in liquid phase. 20 wt.% Pt catalyst on CX were prepared by this technique [29].

Another one-step synthesis, also developed by Alegre et al. [29], uses formic acid (FA, HCOOH) as reductant, in liquid phase. The aim of the FA reduction is to control the reduction speed which is not possible with SB reduction. Indeed, SB-reduced catalysts usually display large Pt particle size distribution (PSD) due to the high reduction speed induced by SB [29,30]. In the above-mentioned study, Alegre et al. synthesized 20 wt.% Pt on CX catalyst *via* FA reduction.

Another one-step method, the synthesis of Pt/C catalysts using a Pt colloid, was developed by Pasqualeti et al. [31]. The method consists in the synthesis of a Pt colloid suspension followed by the addition of a carbon support onto which adsorption of the Pt particles occurs. The aim of the colloid synthesis is to control the Pt particle size while reducing Pt ions with SB, by using tri-sodium citrate (tSC, $Na_3C_6H_5O_7$) as a surfactant. Pasqualeti et al. synthesized 20 wt.% Pt on carbon black (Vulcan XC-72R) catalysts [31].

All these syntheses were reproduced for this work. Some of them were modified in order to change the loading: (i) the CEDI method was repeated up to four times to increase the Pt loading of the catalysts; (ii) the FA reduction synthesis and the colloid synthesis were modified in order to produce 10, 30, and 40 wt.% Pt/CX catalysts in addition to the 20 wt.% Pt/CX catalyst.

Finally, another method based on SEA was performed. Contrary to SEA and CEDI synthesis (the other two method based on SEA), in which reduction step was performed under gaseous hydrogen, this method uses SB reduction in liquid phase. The purpose of this liquid-phase reduction is to fasten the synthesis of highly loaded Pt/CX catalysts obtained by multiple impregnation-reduction methods. These SB-reduced catalysts were compared to SB-reduced catalysts synthesized *via* the one-step synthesis in order to study the differences between one-step deposition and multiple impregnation-reduction steps methods.

This work will focus on these syntheses with the aim of simplifying at best the synthesis process while optimizing the catalyst performances. Note that we decided to focus here on synthesis methods that can be conducted at room temperature and under air, which excludes the commonly used polyol technique [11,10], the latter requiring relatively high synthesis temperatures (393–473 K) and deaerated solutions.

2. Experimental

2.1. Reagents

The solid reagents used in this work were resorcinol $C_6H_6O_2$ (Merck, for synthesis), sodium carbonate Na_2CO_3 (Acros Organics, 99.5% extrapure, anhydrous), dihydrogen hexachloroplatinate (IV) hexahydrate $H_2PtCl_6{\cdot}6H_2O$ (Alfa Aesar, 99.9% metal basis, crystalline), sodium hydroxide NaOH (Acros Organics, extrapure, pellets), sodium borohydride $NaBH_4$ (Merck, fine granular for synthesis), and tri-sodium citrate dihydrate $Na_3C_6H_5O_7{\cdot}2H_2O$ (Merck, EMSURE® for analysis).

The liquid reagents used in this work were formaldehyde solution CH_2O (Sigma Aldrich, ACS reagent 37 wt.% in water, contains 10–15% methanol as stabilizer), hydrochloric acid HCl (Acros Organics, for analysis min. 35 wt.% solution in water), nitric acid HNO_3 (Merck, 65% for analysis), ultrapure water H_2O (18 MΩ cm), formic acid HCOOH, (Merck, 99% for synthesis), sulfuric acid H_2SO_4 (Merck, 96 wt.% Suprapur® for electrochemical measurements or Merck, 98% EMSURE®, for analysis for cleaning solution), hydrogen peroxide H_2O_2 (Merck, 30% Perhydrol®, EMSURE®, stabilized for higher storage temperature, for analysis), and Liquion™ solution (Ion Power, LQ-1105, 1100EW, 5 wt.%).

The gaseous reagents used in this work were nitrogen N_2 (Air Liquide, α1), hydrogen H_2 (Air Liquide, α1), carbon monoxide CO (Air Liquide, N47), argon Ar (Air Liquide, α1), and oxygen O_2 (Air Liquide, α1).

2.2. Syntheses

Carbon xerogel support. CX used in this work was prepared by drying and pyrolysis of a resorcinol-formaldehyde gel. This synthesis is described elsewhere [22]. Briefly, the gel was obtained by polycondensation of resorcinol with formaldehyde in water. The resorcinol/formaldehyde molar ratio, *R/F*, was set at 0.5, the resorcinol/sodium carbonate molar ratio, *R/C*, was chosen equal to 1000 and the dilution ratio, *D*, *i.e.* the solvent/(resorcinol and formaldehyde) molar ratio, was fixed at 5.7. These values led to a CX with a meso-macropore size distribution centered at 80 nm and a BET specific surface area of 567 $m^2\,g_{Pt}^{-1}$. After gelling and aging in an oven at 358 K, the obtained gel was dried under vacuum at 423 K, then ground with a planetary mill (PULVERISETTE 6, classical line, Fritsch) at 400 rpm during 70 min in order to obtain particles with a diameter of a few micrometers