



Control of average particle size of carbon aerogel supported platinum nanoparticles by supercritical deposition



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ABSTRACT

Supercritical deposition was used to synthesize Pt/carbon aerogel (Pt/CA) electrocatalysts. CAs with average pore diameters of 6, 8 and 19 nm (CA6, CA8 and CA19, respectively) were synthesized and impregnated with Pt(cod)me₂ precursor using supercritical carbon dioxide followed by the thermal conversion of the Pt precursor into its metallic form under N₂ atmosphere at various temperatures between 200 and 1000 °C. All of the prepared CAs have high surface areas with very sharp pore size distributions. XRD and TEM results show increased Pt particle size with increasing conversion temperature with a homogenous distribution of nanoparticles on the CA supports. Cyclic voltammetry was used to determine the effect of CA pore properties on electrocatalytic activity. At a conversion temperature of 400 °C, the highest and lowest electrochemical surface area values were obtained for Pt/CA19 and Pt/CA6 of (126 and 36 m²/g, respectively). Furthermore, Pt/CA19 showed good mass activity whereas Pt/CA6 and Pt/CA8 had lower activity values towards the Oxygen Reduction Reaction (ORR). The mass activity values for Pt/CA19 increased with increasing conversion temperature, except for the sample converted at 1000 °C which exhibited the lowest mass activity. The specific activity increased significantly with the conversion temperature up to 600 °C which gave a value six times that obtained at 200 °C. At 800 °C, the specific activity decreased slightly, probably due to a change in the CA structure at this elevated conversion temperature. The Pt/CA19 sample converted at 600 °C exhibited the best performance with a mass activity of 0.1 A/mg_{Pt} and a specific activity of 0.24 mA/cm².

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1. Introduction

Carbon aerogels (CAs) are highly porous carbon materials with high surface areas, low thermal conductivities and high electrical conductivities. CAs are usually obtained by pyrolysis of organic aerogels obtained from a condensation polymerization reaction of formaldehyde and an alcohol such as resorcinol in an aqueous solution with a catalyst. The textural properties of CAs such as pore size, pore volume and surface area can be tuned by changing the conditions in the sol-gel polymerization, curing and pyrolysis steps [1]. Because of these favorable properties, CAs are attracting

increased attention for use in many different applications such as energy storage [2,3], thermal insulation [4,5] and control of harmful emissions by adsorption [6].

Carbon aerogels are also attractive as supports for metals in catalytic applications. There have been quite a few studies reported in the literature on the preparation of CA-supported mono- or bi-metallic nanoparticles including Pt, Pt–Cu and Ru using various methods [7–12]. Carbon-supported Pt nanoparticles are utilized extensively in a wide variety of industries and also as electrocatalysts in polymer electrolyte membrane fuel cells (PEMFCs) due to the excellent activity of Pt towards the oxygen reduction reaction (ORR) [13–15]. The slow kinetics of the ORR are well known [16], and so expensive catalyst layers with very high Pt loadings are required to achieve the desired PEMFC performance. It has been demonstrated previously that there is a strong relationship between the Pt particle size and the electrocatalytic activity [17,18].

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Many studies have shown that the mass activity of the Pt electrocatalyst increases rapidly with increasing particle size up to a certain point (between 1.3 nm and 4 nm) [18–20], beyond which activity declines rapidly with increasing size.

Another important factor that affects catalyst activity in a PEMFC is the support material [21]. The interaction between the support and the metal is of critical importance since it affects parameters such as the nanoparticle shape, morphology and size that are directly related to activity [22,23]. The ideal support should have a high accessible surface area, a suitable pore size and pore volume for efficient ion transport, and high electrical conductivity; CAs are therefore very promising candidates as electrocatalyst supports [5,23,24]. CAs with different pore properties have been investigated previously as electrocatalyst supports. Du et al. conducted a study in which CAs with different mesoporous structures were loaded with Pt using the ethylene glycol reduction method, and the resulting composites had ORR activities higher than those of commercial Pt/C electrocatalysts. The ORR activity of the composites correlated well with the average pore size of the CAs, and the highest activity was achieved with the CA with the largest mesopores [11]. In another study conducted by Marie et al., two different CAs were loaded using two different Pt precursors (anionic and cationic) via wet impregnation. The authors did not observe any effect of the CA pore size on activity, however, the samples prepared using the anionic Pt precursor had higher activities than the ones prepared with the cationic precursor [12].

There are no studies in the literature on the effect of Pt particle size on electrocatalytic activity for CA supports. However, considering the previous studies in the literature using other carbonaceous supports, such an effect may also exist for CA-supported Pt nanoparticles. Therefore, there is a need to develop techniques which enable tight control of the metal particle size on CAs to test this hypothesis. Moreover, such techniques would also be beneficial for the application of metal supported CAs in size-sensitive reactions such as reforming of ethylene glycol, hydrogenation of cinnamaldehyde, and oxidation of methanol and ethanol [25–29].

Supported metal nanoparticles can be prepared using various different techniques such as ion-exchange, wet impregnation, sol-gel, and chemical vapor deposition [30–36]. These conventional techniques are used widely, however it is quite challenging to control the metal nanoparticle distribution, nanoparticle size, size distribution, metal loading, and nanocrystal orientation with these techniques [37]. The supercritical deposition (SCD) technique is an emerging approach for the preparation of supported nanoparticles that has several advantages over its counterparts [22,38–45]. SCD is especially suitable for processing of CAs since the low capillary stresses in the supercritical fluid prevent the collapse of the pores of CAs during the adsorption and solvent removal stages. Furthermore, a very homogenous distribution of metal nanoparticles can be achieved with SCD, whereas agglomeration usually occurs in other preparation techniques such as wet impregnation and chemical vapor deposition [12,24,46]. Another benefit of SCD is that the metal loading can be controlled by using isotherm data.

In this study, we demonstrate a way to control the average size of Pt nanoparticles on CAs using SCD, and we show that the technique is effective for CAs with different average pore sizes. The effects of the CA pore size at a narrow pore size range (6 and 8 nm) and at a higher pore size (19 nm) on the electrocatalytic activity of the Pt/CA composites, and the effects of the Pt particle size on the ORR activity, were also investigated. The physical and electrochemical properties of the Pt/CAs were characterized using a combination of N_2 physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA), Raman spectroscopy and transmission electron microscopy (TEM) techniques.

2. Experimental

2.1. Materials

Resorcinol (99%) and acetone (99.9%) were obtained from Sigma-Aldrich. Sodium carbonate (99.99%) was purchased from Merck and formaldehyde (36%) was purchased from Lachema. Dimethyl(1,5-cyclooctadene)platinum(II) ($Pt(cod)me_2$, 99%, MW = 333.33 g/mol) was purchased from STREM Chemicals, Inc. The chemicals were used as-received without any further purification. Carbon dioxide, nitrogen and oxygen (all at 99.998% purity) were purchased from Messer Aligaz. Water was distilled and deionized before usage.

2.2. Synthesis of resorcinol formaldehyde aerogels (RFAs) and carbon aerogels (CAs)

RFAs were synthesized by the reaction of resorcinol with formaldehyde in water in the presence of an alkali catalyst (Na_2CO_3) as described elsewhere [1]. In order to obtain different pore sizes, different resorcinol/catalyst (R/C), and resorcinol/water (R/W) ratios were used while keeping the resorcinol/formaldehyde (R/F) ratio constant during the synthesis. A solution was prepared using the desired amounts of resorcinol, water, catalyst and formaldehyde, and this was stirred for 15 min. The prepared solution was then transferred into airtight tubes. The tubes were kept for one day at room temperature, one day at 50 °C, and then three days at 90 °C to complete the gelation and curing processes. Afterwards, the samples were removed from the tubes and placed in an acetone bath for solvent exchange and kept there for three days. Acetone remaining in the gel pores was then removed by supercritical extraction using $scCO_2$ at 13.8 MPa and 50 °C (Applied Separations Spe-ed SFE). As a result, RFAs with different pore sizes were obtained. CAs were then obtained by the pyrolysis of the RFAs in a tube furnace (Model F1125 Thermolyne) at 1000 °C for 6 h under flowing N_2 (100 cc/min).

2.3. Preparation of $Pt(cod)me_2/CA$ composites via supercritical deposition

Fig. 1 is a schematic of the experimental setup used for the supercritical deposition experiments. Predetermined amounts of CA and $Pt(cod)me_2$ were placed in a custom-made high pressure stainless steel vessel equipped with two sapphire windows (57 mL internal volume) along with a magnetic stirrer to ensure adequate mixing of the precursor and $scCO_2$. A syringe pump (ISCO Model

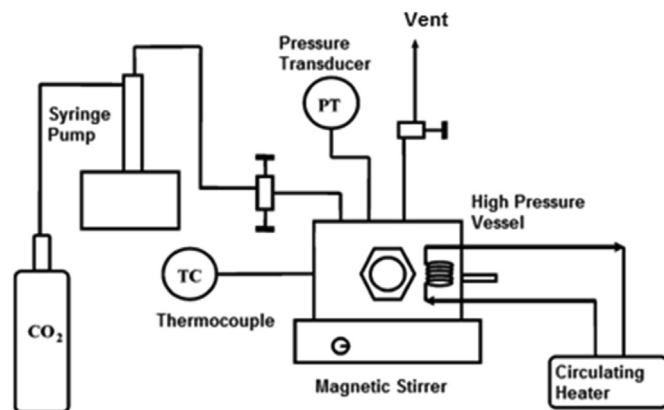


Fig. 1. Experimental setup.

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