



Stability of platinum nanoparticles supported on surface-treated carbon black



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ABSTRACT

Platinum nanoparticles supported on carbon black (CB) are used as electrocatalysts in polymer electrolyte fuel cells, and their stability is important for the durability of the catalyst system. Here, we investigated the stability of Pt nanoparticles supported on surface-treated CB with a thermochemically developed surface nanostructure. The protruding structure of surface-treated CB was able to support Pt nanoparticles synthesized via the sodium tetrahydroborate (NaBH₄) reduction of hexachloroplatinic(IV) acid hexahydrate (H₂PtCl₆·6H₂O) with polyvinylpyrrolidone (PVP). The dependence of Pt stability on the deposition locations on the CB surface was examined using in situ transmission electron microscope observations during heating up to 800°C. We found that the protruding parts on the CB surface function as local sites for stably supporting Pt nanoparticles. Hence, we suggest that the stability of the Pt nanoparticles can be improved using the CB surface nanostructure.

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1. Introduction

Platinum nanoparticles behave as electrocatalysts in polymer electrolyte fuel cells (PEFCs), and carbon black (CB) is widely used to support them [1]. A typical PEFC catalyst layer consists of Pt nanoparticles of diameter less than 5 nm dispersed on the CB support, and catalyst degradation occurs during the PEFC operation owing to the sintering of Pt nanoparticles and oxidation of the CB support [2]. Even though many approaches have been proposed to enhance the durability of the Pt catalyst system [1,3], further improvements are needed for both catalyst particles and support materials.

CB is a carbonaceous particulate material produced by partial combustion or thermal decomposition of hydrocarbons [4]. Nascent particles are thought to form from molecular precursors such as polycyclic aromatic hydrocarbons. Because of its formation mechanism, the primary particles are nearly spherical. Several primary particles coalesce into an aggregate which is the basic morphological unit of CB. Depending on the intended applications, the

physical and chemical characteristics of CB are modified by controlling the size, aggregate structure, internal crystalline structure, and surface chemistry. In a PEFC catalyst system, CB is employed as a catalyst support because of its good electrical conductivity, high surface area, and low cost [1]. In addition to these favorable characteristics, it would be more beneficial if we could add more functions to CB to enhance the stability of the supported Pt nanoparticles.

The authors investigated the kinetics of the methane and alcohol thermal decomposition under the environment where CB existed, and found the evolving surface nanostructure of CB due to continuous deposition of carbon atoms on the CB surface [5–8]. We observed that a graphitic sheet-like structure was developed and a protruding nanostructure formed over the CB surface. We have shown that surface structure development using carbon deposition is applied for a surface treatment process to enhance the oxidation resistance of CB [8]. An earlier study [9] has also demonstrated that the physical structure of the carbon surface affects the dynamic behavior of the supported catalyst nanoparticles. Thus, we expect the nanostructure of the CB surface, which is developed on initially spherical CB, to positively affect the Pt nanoparticles behavior by stably supporting them and inhibiting sintering.

To examine the deposition state of Pt nanoparticles on the support material, transmission electron microscope (TEM) observation is a useful technique [10]. In situ observations during sample heating help us to understand the dynamic behavior of nanoparticles [9,11–16]. In particular, when the support material surface is inho-

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mogeneous, the differences in the stability characteristics of the Pt nanoparticles arising from the nature of deposition sites are of interest. In such cases, in situ TEM observations are well suited to observe nanoscale phenomena.

In the present work, the stability of Pt nanoparticles supported on surface-treated CB was investigated. The CB surface nanostructure was built as described in our previous papers [5–8]. We used two types of Pt nanoparticles with respect to dispersion state on CB surface: agglomerated and monodispersed particles. The dynamic behavior of the Pt nanoparticles during heating was examined by means of in situ TEM observation. TEM images were obtained and analyzed to study the stability characteristics depending on the deposition sites on the CB surface. In addition, the interaction of Pt and CB particles during the Pt deposition process and the effect of the dispersing agent on Pt sintering are discussed.

2. Experimental

2.1. Carbon samples

Commercial CB SB905 (Asahi Carbon, Japan) was used because of its superior homogeneity in particulate properties. The mean diameter of the primary particle is 15 nm and the specific surface area is 212 m²/g. The sample was stored in a desiccator after receiving from the manufacturer and was used as received.

2.2. Surface treatment of CB

We treated the CB surface following the thermochemical process developed in our previous studies [5–8]. The samples were placed in a vertical quartz tube reactor heated by an electric tube furnace. The gaseous carbon source (methane or ethanol vapor) was supplied with the carrier gas into the reactor. The duration of the reaction was adjusted to control the degree of surface nanostructure development.

2.3. Platinum nanoparticle synthesis and deposition on CB

After completing the CB surface treatment, Pt nanoparticles supported on CB (Pt/CB samples) were prepared via an aqueous process. The synthesis procedure is shown in Fig. 1. For the deposition of Pt agglomerates on CB, we simply mixed a commercial Pt colloid and a CB dispersion (Fig. 1(a)). Because it is difficult to obtain nonagglomerated Pt particles with this method, we used the sodium tetrahydroborate (NaBH₄) reduction method to prepare monodispersed Pt particles (Fig. 1(b)) [17]. The Pt precursor, hexachloroplatinic(IV) acid hexahydrate (H₂PtCl₆·6H₂O), was dissolved in water to obtain a solution of 4.0 mM. Polyvinylpyrrolidone (PVP) was used to stabilize the nanoparticles, and a 12 mM (monomer unit) water solution was added to the Pt precursor solution. Sodium tetrahydroborate (NaBH₄) was then added to the solution to reduce the Pt salt. CB was placed into water followed by ultrasonication; the CB suspension was then mixed with the Pt precursor solution. The mixture was vigorously stirred using a magnetic stirrer, and the Pt nanoparticles were synthesized. Subsequently, centrifugation was performed to remove the large agglomerated particles. To analyze the as-synthesized well-dispersed Pt particles, we also prepared a Pt suspension without adding CB.

The size distribution and zeta potential of the Pt nanoparticles in water were measured using an ELSZ-1000 zeta potential & particle size analyzer (Otsuka electronics, Japan). The particle size analysis was based on dynamic light scattering (DLS) scheme.

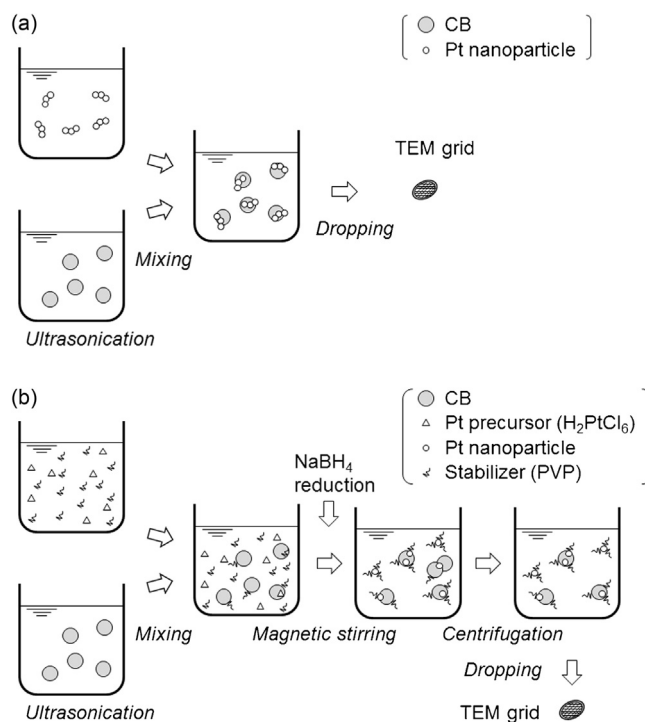


Fig. 1. Schematic illustration of the aqueous sample synthesis procedures: (a) colloid method, and (b) NaBH₄ reduction method.

2.4. Transmission electron microscopy

To observe the Pt/CB samples during heating, a JEM-2100F transmission electron microscope (JEOL, Japan) was used. The microscope was operated at an acceleration voltage of 200 kV. The samples were deposited on a Cu TEM grid (200 mesh) with an amorphous carbon film (U1003, EMJapan, Japan) and heated with a heating holder (Gatan model 652). The TEM images were analyzed with the ImageJ software [18].

3. Results and discussion

3.1. Dynamic behavior of agglomerated Pt nanoparticles

We used the aqueous suspension of agglomerated Pt nanoparticles to prepare samples for the first TEM heating experiment. The primary particle diameter was about 3 nm based on the TEM observations, and the number-averaged diameter evaluated by DLS was 23 nm (Fig. 2). This suggested that the Pt nanoparticles were not monodispersed but already agglomerated when in suspension. We performed TEM observations of the Pt nanoparticles deposited on CB and calculated the radius of gyration R_g from the obtained images [19,20]. The radius of gyration of the agglomerates consisting of primary particles is

$$R_g^2 = \frac{\sum_i (r_i - r_c)^2 m_i}{\sum_i m_i}, \quad (1)$$

where $r_i - r_c$ is the distance from the center of mass of an agglomerate to a primary particle i , and m_i is the mass of primary particle i . To apply this R_g calculation to the TEM image analysis, we used the image area of the particles instead of mass. Although this is typical in TEM image analysis [19,20], the obtained value is based on 2D data, whereas the data obtained by DLS are intrinsically 3D. The averaged $2R_g$ was about 18 nm and close to the mean diameter of 23 nm based on DLS, which means that remarkable agglomeration did not occur during deposition.

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