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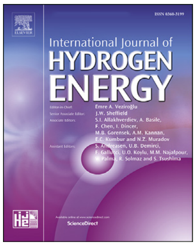

Palladium nanoparticles from surfactant/fast-reduction combination one-pot synthesis for the liquid fuel cell applications

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ABSTRACT

We report a facile one-pot synthesis of well-dispersed Pd nanoparticles on a carbon nanofiber (CNF) support, achieved via the unique sequential processes of supramolecular self-assembly and fast reduction of the Pd source. Pd ions attached to the sulfate ends of sodium dodecyl sulfate (SDS) molecules self-assembled on a CNF, and subsequent fast reduction suppressed particle coarsening, in contrast to the slow reduction processes in previous works. The particle size and dispersion uniformity were comparable to those of particles synthesized by combined SDS/high-energy irradiation. The Pd nanoparticles prepared using the present one-pot approach were superior or comparable to those obtained using non-one-pot approaches in previous works in terms of electrocatalytic activity and long-term stability in the electrooxidation of liquid fuels at the anodes of direct formic acid, direct methanol, and direct ethanol fuel cells.

Introduction

The fuel cell has been actively investigated for decades as a solution to energy and environmental issues [1]. The direct formic acid fuel cell (DFAFC), direct methanol fuel cell (DMFC), and direct ethanol fuel cell (DEFC) are known to be most suitable for portable electronic devices [2–4], due to facile device construction, high energy conversion efficiencies, low operation temperatures, convenient storage (liquid fuels), and generation of nonhazardous byproducts [4,5]. One of the key requirements for such fuel cells is the development of electrode catalysts that enable high energy densities [4,6,7]. Pt-based anode catalysts are used most frequently due to their unique electrocatalytic properties [8], but high costs and limited Pt reserves have hindered commercial applications [9,10].

Recently, Pd-based catalysts have been reported as more cost-effective, alternative catalysts. Experimental and theoretical studies have indicated that their activities and electrode poisoning resistance against carbon monoxide are comparable to those of Pt-based catalysts [11–13]. Nevertheless, the electrocatalytic activity and durability of Pd-based

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catalysts still require further improvement. To resolve these issues, alloying has been frequently employed [14–20], but this approach introduces undesirable process complexity. The nanoscale dispersion of Pd nanoparticles on conductive nanocarbon supports [21–23] with large specific surface areas [24] has also been studied. However, the formation of Pd complex ions requires rather complicated reduction or doping techniques [5,15,25,26], which prevent the use of simple, cost-effective one-pot synthesis methods. Although high loading of Pd nanoparticles (approximately 20 wt%) on various support materials has been reported occasionally [5,27], there remains considerable scope for further improvements in particle size, nanoscale dispersion, and performance, as will be shown here.

The aforementioned issues may originate from the Pd loading steps, where *slow* reduction processes have been customary, usually assisted by a *stabilizer*. This approach was inevitable in the absence of an appropriate surfactant, as the stabilizer action might not compensate for the rapid increase in Pd atom concentration driven by excessively fast reduction. Nevertheless, it is rather surprising that such an approach has been extended to some cases in which an effective surfactant (*e.g.*, the supramolecular self-assembly agent sodium dodecyl sulfate (SDS)) [28] was used. In such cases, as atomic-scale dispersion of Pd ions on the support was achieved, the stabilizer might be unnecessary [29,30]. Slow reduction processes, such as hydrothermal or electrochemical methods [29,30], are orders of magnitudes slower than processes using fast reducing agents, *e.g.*, $NaBH_4$. Such slow reduction kinetics might result in a correspondingly slow increase in the concentration of neutral Pd atoms, and hence, decrease supersaturation [31]. We suppose that this scenario should lead to particle coarsening, from the perspective of the well-known nucleation theory (see chapter 9 in Ref. [32]). Such a possibility was supported by the reduction of SDS-dispersed Pd ions by high-energy irradiation, *i.e.,* gamma rays, which led to a somewhat fast reduction, and hence, produced fine Pd particles [33]. We also suppose that the thermal or electrochemical energy in the hydrothermal/electrochemical reduction might further accelerate particle coarsening by enhanced atomic diffusion during Ostwald ripening or by accelerated particle sintering, respectively [34–36].

Thus, we propose that adopting a *fast* reducing agent, *e.g.*, $NaBH_4$, in conjunction with SDS, might enable a much finer particle size to be produced and better electrochemical activities in liquid fuel cell applications, with the added benefit of a simple *one-pot* approach. However, such an intriguing possibility has not been investigated so far. Another important issue is particle dispersion on the support material. The SDS/fast-reduction approach using gamma-ray irradiation [33] not only achieved particle refining, but also uniform dispersion. However, it has yet to be clarified whether such uniform dispersion can also be realized via similar approaches that adopt *chemical* means for the fast reduction process rather than the irradiation; indeed, one might suppose that the drastically differing natures of the two reduction processes might possibly result in accordingly differing particle dispersions. Still another important issue was the durability: it was not reported yet, at least in the SDS-derived Pd nanocatalysts for liquid fuel cell applications. In the present study, we investigated these important issues by employing the one-pot synthesis on a carbon nanofiber (CNF) support for DFAFC, DMFC, and DEFC anode catalyst applications.

Experimental

Materials

Herringbone-type CNF was purchased from VINAtech Co. Palladium(II) nitrate dehydrate, SDS, sodium borohydride ($NaBH_4$), and 5 wt% Nafion solution were purchased from Sigma-Aldrich Co.

Synthesis of Pd/CNF and Pd/SDS-CNF catalysts

In a typical procedure for Pd/SDS-CNF, 100 mg of CNF was dispersed ultrasonically in 100 mL of deionized (DI) water. Then, 50 mg of SDS was added to the resulting CNF suspension, and the mixture was stirred for 30 min. Subsequently, palladium(II) nitrate dehydrate was dissolved in the aforementioned solution, which was allowed to stir for 1 h. The Pd content was 20 wt%. The reduction reaction was conducted by admixing with a $NaBH_4$ solution. The reaction mixture was filtered through a 200 nm cellulose acetate membrane filter, and then washed with a mixture of ethanol and DI water. The final product was dried at 60 °C. For comparison, Pd/CNF was prepared by the same procedure, without the SDS coating process.

Physical characterization

The nanostructures of the synthesized samples were analyzed by high-resolution transmission electron microscopy (HR-TEM, Titan). The crystalline structure and average particle size were determined by X-ray diffraction (XRD) analysis (Bruker). The Pd particle size was calculated from the (220) diffraction peaks. Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was conducted to estimate the Pd loading on the CNF support.

Electrochemical analysis

All electrochemical measurements were conducted using a VSP potentiostat/galvanostat (Biologic Co., France). A Hg/Hg_2SO_4 electrode and Pt wire were used as the reference electrode and the counter electrode, respectively. Prior to drop-coating the Pd catalyst on a glassy carbon electrode (GCE, 3 mm in diameter), the electrode surface was polished successively with 1 μm and 0.05 μm alumina abrasive powders, and then rinsed twice with an aqueous solution of isopropyl alcohol. The rinsed GCE was dried by blowing with nitrogen gas. The Pd catalyst (3 mg) was ultrasonically mixed with isopropyl alcohol (0.5 mL), DI water (0.5 mL), and Nafion solution (50 μL). A 12 μL droplet of the suspension was dropped onto the GCE and was dried by blowing with nitrogen gas. The loaded amount of Pd was 0.098 mg/cm^2. DFAFC measurements were performed in a solution of 0.5 M H_2SO_4 containing 0.5 M formic acid. The DMFC and DEFC measurements were conducted in a 1 M KOH solution containing 1 M methanol and 1 M ethanol, respectively.

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