One-pot synthesis of carbon-supported monodisperse palladium nanoparticles as excellent electrocatalyst for ethanol and formic acid oxidation
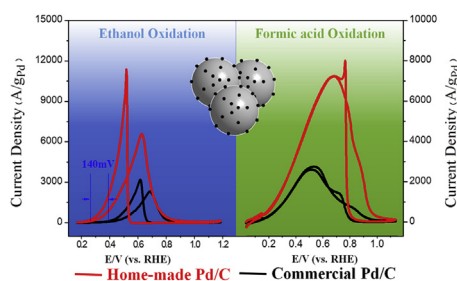
Qiang Wang, Yuxiang Liao, Heyou Zhang, Jun Li, Wei Zhao[*], Shengli Chen[*]

Hubei Key Laboratory of Electrochemical Power Sources, Department of Chemistry, Wuhan University, Wuhan 430072, China

HIGHLIGHTS

- Facile surfactant-free synthesis of carbon-supported monodisperse Pd (Pd/C).
- Excellent electrocatalytic performance for formic acid and ethanol oxidation.
- Different particle size effects of Pd on the formic acid and ethanol oxidation.
- Adsorbed hydroxyl groups play important roles in the ethanol oxidation on Pd.

GRAPHICAL ABSTRACT

ABSTRACT

Electrocatalysts of ultrafine and surface-clean nanoparticles uniformly dispersed on high-surface-area conducting supports are among the prime requests for large-scale application of fuel cells. We report a facile one-pot synthesis of carbon-supported monodisperse and ultrafine Pd nanoparticles (Pd/C) in N,N-dimethylformamide by using amine—borane as reducing agent in the absence of any surfactants. The ultrasmall size, monodispersity and surfactant-free surface of Pd nanoparticles make the resulted Pd/C catalyst exhibit excellent electrocatalytic performance toward the oxidation of organic fuels. For formic acid oxidation reaction, it exhibits a similar onset potential to that of the commercial Pd/C (BASF) but about 2.6 times increase in current density, which can be attributed to the increased electrochemically surface area (ECSA); while for ethanol oxidation, it shows about 140 mV negative shift of the onset potential as well as the current increase much beyond that expected by the increased ECSA, indicating that the reduction of Pd particle size not only increases the ECSA, but also enhances the intrinsic activity of surface Pd atoms. The different activity enhancing behaviors for the formic acid and ethanol oxidation have been discussed in terms of the reaction mechanisms. Chronoamperometric measurements show that the home-made Pd/C is also much more durable.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Thanks to the high energy and power density and low environmental pollution, direct liquid fuel cells that directly electro-oxidize small organic molecules (SOMs) (e.g., methanol, ethanol, formic acid) [1–6] in the anode have attracted a great deal of

attention [7–9]. Especially, formic acid and ethanol, which have lower toxicity, higher availability and energy density relative to methanol, have been investigated extensively in recent years as the anodic fuels. For instance, twelve electron transfers can be generated when an ethanol molecule is completely oxidized, which leads to an singularly high energy density of ~29.7 MJ/kg. But in situ Fourier transform infrared spectroscopy (FTIR) result shows that the selectivity from ethanol to CO_2 is relatively low [10,11].

Highly active catalyst for the electro-oxidation of the anode fuel is one of the key requirements for the practical application of a direct liquid fuel cell. Palladium, which is relatively cheap and abundant among various precious metals, has desirable electro-catalytic activity for SOMs and receives a wide range of applications [12–14]. The performance of fuel cells relies on the size, surface cleanness and dispersity of catalysts [15,16]. Several studies have reported palladium nanoparticle size and dispersity effects in the electro-oxidation of formic acid and ethanol [12,17]. Binding energy shifts and d-band vacancy changes were applied to rationalize the changes in specific activity with particle size [18,19]. Meanwhile, small nanoparticles show great catalytic activity because of large surface area and a number of edge and corner atoms [20–26]. In general, nanoparticles should be produced as small as possible for the purpose of high surface area. However, smaller metal nanoparticles own higher surface energy, which usually result in serious aggregation in order to minimize the total surface energy [27]. The aggregation of metal nanoparticles may be prevented by using surfactants that are adsorbed on nanoparticles surface [28]. Unfortunately, the surfactants molecules could severely limit the catalytic properties because they are difficult to be completely removed due to the strong interaction with metal [29].

Dry impregnation method has been commonly used to prepare supported metal nanoparticle catalysts without using the surfactants. In this method, the metal precursors and high specific-surface-area support are first dispersed in a solvent; the suspension is then heated while stirring to allow the solvent to evaporate till a slurry is formed, which is dried and finally subject to reduction with reducing gas such as H_2 at relatively elevated temperatures. As well as the cumbersome process, this traditional method also suffers from sintering and poor distribution of catalyst particles [30].

In this work, we report a facile one-pot and stabilizer-free preparation of monodispersed ultrafine palladium nanoparticles supported on Vulcan XC-72 and their excellent electrocatalytic activity toward ethanol and formic acid oxidation. The synthesis relies on the use of DMF as solvent and amine–borane as the reducing agent. The synthesis process is schematically presented in Fig. 1.

The availability of a free electron pair of DMF makes it strongly interact with carbon particles [31], which does not only allow the well dispersion of carbon particles, but also facilitates the formation of a DMF-rich region around carbon particles (Fig. 1). Accordingly, the Pd (acac)$_2$ (acac = acetylacetone) precursor can be enriched around carbon particles. In addition, as a weak base with amide group, DMF around the carbon particles can anchor the produced Pd atoms/clusters and help the formation of monodisperse Pd nanoparticles on Vulcan XC-72 support [32,33]. The amine–borane complexes are effective reductants for producing monodisperse metal or alloy nanoparticles [34–39]. In comparison with the usually used reducing agents such as borohydrides, amine–borane complexes have a relatively mild reducing ability, which can avoid the overgrowth of nanoparticles. Furthermore, their reducing abilities can be regulated by changing the alkyl substitution on nitrogen [39]. Here, we find that N,N-diethylaniline-borane can be an appropriate reductant for Pd (acac)$_2$ in DMF to yield highly disperse Pd nanoparticles.

2. Experimental

2.1. Chemicals and materials

Ethanol (C$_2$H$_5$OH, >99.8%), N,N-dimethylformamide (C$_3$H$_7$NO, ≥99.5%) were purchased from Sinopharm Chemical Reagent Co., Ltd., N, N-diethylaniline borane (C$_{18}$H$_{15}$N·BH$_3$, >98%) was purchased from TCI Shanghai Co., Ltd. Palladium acetylacetonate (Pd (acac)2, >98%) was purchased from Kunming Sino-Platinum Co., Ltd. All chemicals of analytical grade were used without further purification. Milli-Q ultrapure water (Millipore, >18.2 MΩ cm) was used throughout the experiments. The commercial Pd/C catalyst (20 wt %) from BASF was used as the reference sample to evaluate the electrocatalytic performance of the catalyst prepared in this study.

2.2. Preparation of Pd/C catalyst

Carbon-supported monodisperse Pd nanoparticles (22 wt%) were synthesized by mixing the 30 mg Pd (acac)$_2$, 25 mg Vulcan XC-72 and 25 mL DMF in the flask. After ca. 60 min' sonication and then the mixture was stirred 10 min, 200 mg N, N-diethylaniline borane was fast injected in the flask at the room temperature. An hour later, the product was collected by centrifugation at 8000 rpm for 5 min. The obtained catalyst was further washed twice in ethanol and dried in vacuum drying oven at 60 °C for 6 h.

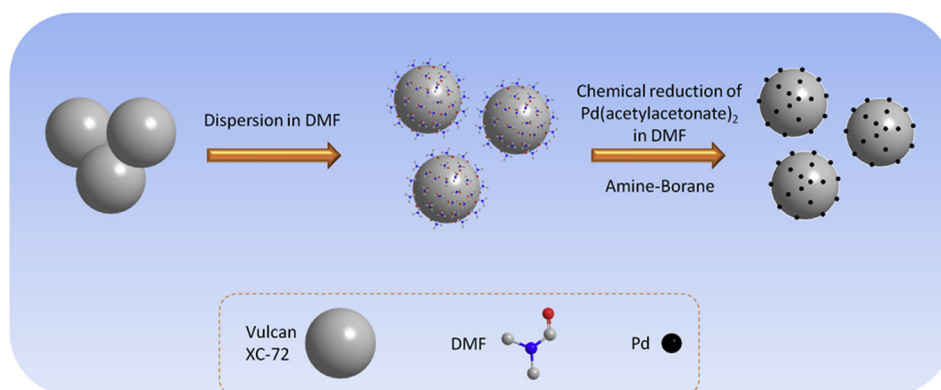**Fig. 1.** Schematic illustration of the synthesis process of Pd/C catalyst in DMF.