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# Pd nanoparticles supported on PDDA-functionalized carbon black with enhanced ORR activity in alkaline medium

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## ABSTRACT

Pd/C catalyst with small particle size, high dispersion and high wt.% of metal was in situ synthesized by a simple aqueous phase reduction method. Poly(diallyldimethylammonium chloride) PDDA-functionalized carbon black was used as a support material for the in situ deposition of Pd nanoparticles by means of electrostatic attraction. The catalysts were characterized by transmission electron microscopy, X-ray diffractometry and X-ray photoelectron spectroscopy, cyclic voltammetry and rotating disc electrode test. The results indicated that Pd nanoparticles with an average size of 2.09 nm were uniformly dispersed onto the carbon black with a metal weight percentage of ~30 wt.%. The prepared Pd/C catalyst has showed remarkably larger electrochemical surface area and higher and more stable ORR activity as compared to commercial Pd/C catalyst and commercial Pt/C catalyst in alkaline media, which was believed to be a promising alternative to Pt-based catalyst used in alkaline fuel cell.

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## Introduction

Fuel cells have been widely recognized as one of the cleanest and most efficient alternatives to conventional heat engines for generating electricity with near zero pollutant emission, high efficiency and low noise [1–8]. Today, most of the low-temperature PEM fuel cells use hydrogen exclusively as the fuel, but hydrogen is still expensive at the moment and

difficult to be stored, not to mention transport and distribution issues as compared to the logistic hydrocarbon fuels. Thus, direct methanol fuel cells (DMFCs) have attracted more and more attention, especially for small portable power application, due to the use of liquid methanol with acceptable gravimetric and volumetric energy density [9,10]. However, the full potential of DMFCs has not yet been realized due to the methanol crossover through the polyelectrolyte membrane, sluggish kinetics of oxygen reduction reaction (ORR) and

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methanol oxidation reaction (MOR), high cost and particularly sensitive to CO poisoning of platinum (Pt) and Pt alloys catalyst. The slow kinetics of ORR at the cathode results in a large overpotential and low current density. Unlike in acidic media, the kinetics of both methanol oxidation reaction and oxygen reduction reaction in alkaline media is much faster [11,12], and non-precious metal catalyst may be used to reduce the cost of the fuel cell [13,14]. Moreover, fuel crossover is reduced because it is opposite to electro-osmotic drag direction and CO positioning is less an issue in alkaline environment [15].

Palladium (Pd) exhibits roughly half the price of Pt and is 200 times higher in reserve than Pt (0.6 ppb vs. 0.003 ppb) in the earth's crust, which makes it more attractive for large-scale fuel cell applications. Although Pd electrode exhibits no electrocatalytic activity for alcohol oxidation (AO) in acidic media, it has demonstrated competitive alcohol oxidation activity and slightly better ability to break C–C bond of ethanol in alkaline media as compared to traditional Pt-based catalysts [16–21]. Besides, it has recently been demonstrated that the activity of Pd nanoparticles toward ORR surpasses that of Pt nanoparticles in alkaline environment [22–25]. Therefore, the high activity for certain reactions and good resistance to CO poisoning make Pd a good candidate for DMFC application. However, palladium nanoparticles with small size and finely metal dispersion on carbon support are difficult to be achieved, especially when with high metal loading, because metallic particles tend to sinter together due to weak interactions between the metal and the carbon. Mamlouk et al. have prepared a series of carbon supported Pd nanoparticles using different reducing agent, including ethylene glycol, formaldehyde and sodium borohydride. The average sizes of all prepared Pd nanoparticles with different reducing agents are more than 5 nm [26]. Pd nanoparticles with a smaller size and a high metal loading are desirable for good catalytic activity. Hence, it is imperative to develop a convenient and efficient synthesis method to prepare highly dispersed nano Pd catalyst with a high metal weight percentage for “tough” reactions such as ORR and MOR.

Self-assembly method is a well-known technique in the preparation of well-ordered nano-structures [27]. Using this method, Jiang et al. have reported the application of polycation, poly(diallyldimethylammonium chloride) PDDA, to stabilize Pt nanoparticles. The PDDA stabilized Pt can not only be self-assembled onto the Nafion electrolyte

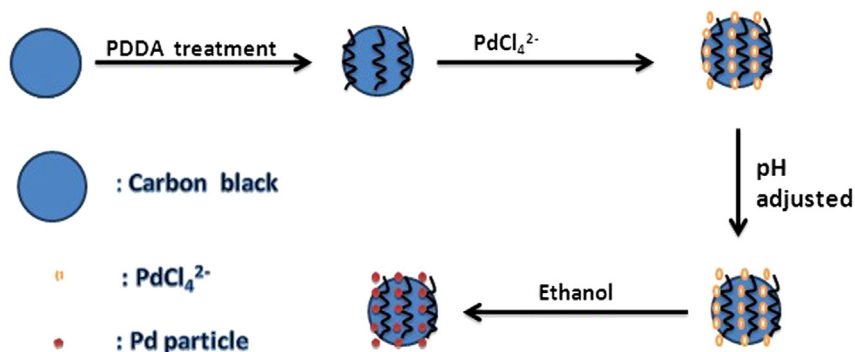
membrane, forming an electrochemically active monolayer on the Nafion membrane surface to block the methanol permeability, but also can serve as an excellent homogeneous catalyst, showing interesting catalytic properties [28–30]. In the present study, carbon supported Pd catalyst with a high wt.% and finely dispersed nano size was prepared in the presence of PDDA by the self-assembly method. The whole reduction reaction was carried out in an aqueous solution, which is simple, easy to be scaled up and environmentally friendly. The positive charged groups of PDDA were expected to act as anchor sites and enable the subsequent *in situ* formation of Pd particles. The prepared catalyst was characterized by XRD, TEM and XPS, and the electrochemical activity was also examined.

## Experimental

Poly diallylmethylammonium chloride (35 wt.%), palladium (II) chloride (5 wt.% in 10 wt.% HCl solution), ethanol and Nafion solution (5 wt.%) were purchased from Sigma Aldrich. All the chemicals were used as received without any purification. Commercial 20% Pd/C catalyst from Alfa Aesar (denoted as AA Pd/C) and 40% Pt/C from Johnson Matthey (denoted as JM Pt/C) were used as reference.

### Synthesis of Pd/C catalyst

As shown in Scheme 1, Pd/C catalysts were prepared by reducing the metallic ions with alcohol in the presence of ionic polymers poly(diallylmethylammonium chloride) PDDA. 42.6 mg of carbon black (Vulcan XC-72R from Cabot, refluxed in 2 M HCl and 5 M HNO<sub>3</sub> separately before use) was ultrasonically dispersed in 80 ml, 0.002 mol/L of PDDA solution and then transferred into a three-neck flask under intensive stirring. 8 ml, 0.02 mol/L of PdCl<sub>2</sub> (10 wt.% HCl) solution was added and vigorously stirred for another 30 min. 60 ml of EtOH was subsequently added into the solution. The pH of the solution was then adjusted to 8.5 by adding 0.5 M of NaOH solution drop by drop. At last, the solution was refluxed at 85 °C in a temperature-controlled oil bath for 5 h. After the sample was cooled down to room temperature, the prepared catalyst was filtrated, fully washed with DI-water and then dried at 80 °C.



Scheme 1 – The schematic Pd/C preparation.

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