



Short communication

Oxygen reduction reaction on carbon-supported palladium nanocubes in alkaline media



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ARTICLE INFO

Article history:

Received 2 December 2015

Received in revised form 21 December 2015

Accepted 22 December 2015

Available online 6 January 2016

Keywords:

Oxygen reduction

Pd nanocubes

Supported catalysts

Electrocatalysis

ABSTRACT

Carbon-supported Pd nanocubes with the size of 30, 10 and 7 nm were prepared and their electrocatalytic activity towards the oxygen reduction reaction (ORR) in alkaline solution was studied. For comparison carbon-supported spherical Pd nanoparticles and commercial Pd/C catalyst were used. The catalysts were characterised by transmission electron microscopy, electro-oxidation of carbon monoxide and cyclic voltammetry and the ORR activity was evaluated using the rotating disk electrode method. The ORR on all studied Pd/C catalysts proceeded via four-electron pathway where the rate-limiting step was the transfer of the first electron to O₂ molecule. The specific activity of Pd nanocubes was more than two times higher than that of spherical Pd nanoparticles and increased with increasing the particle size.

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1. Introduction

Platinum is the best electrocatalyst among pure metals for oxygen reduction reaction (ORR) and palladium has proven to be suitable substitute for it as both metals are in the same group in the periodic table, have same crystal structure, similar atomic size and the ORR proceeds via same reaction mechanism [1,2]. Jiang et al. found that on Pd catalysts the ORR in alkaline solution exhibits particle size effect as the specific activity increases continuously by a factor of three with increasing particle size from 3 to 16.7 nm, while the mass activity showed a maximum at Pd particle size of 5 nm [3]. It was suggested that the increased adsorption of OH⁻ decreases the number of active sites for ORR, thus decreasing the specific activity. The mass activities increased with decreasing particle size as larger number of Pd atoms participated in the surface catalysed reactions and in combination with specific activity the optimum Pd particle size was suggested to be around 5 nm. The same workgroup has also reported that in alkaline media Pd nanoparticles (PdNPs) have higher activity towards the ORR than Pt nanoparticles (PtNPs), which was explained by the differences in surface oxidation [4]. Similar results were reported for graphene-supported PdNPs and PtNPs [5].

On both Pd and Pt the electroreduction of oxygen is a structure-sensitive reaction [2]. Kondo et al. showed that in perchloric acid solution the activity of Pd single-crystal facets rises in the following order: Pd(110) < Pd(111) < Pd(100) [6]. In addition, it has been shown that oxide film is not relevant to the ORR on n(111)-(100) series of Pd at

0.9 V vs RHE in perchloric acid and (111) terrace is the active site for ORR [7]. Cai et al. treated particles in Br⁻-containing solution to reduce surface roughness and to increase Pd(111) surface sites, as a result a significant improvement in specific activity and mass activity was observed as compared to untreated particles [8]. The reduction of oxygen on unsupported Pd nanocubes has been studied in both acidic and alkaline solutions and enhanced ORR activity of cubic PdNPs has been demonstrated, which has been suggested to arise from the Pd(100) single-crystal facet [9–14]. Shao et al. showed that carbon-supported Pd nanocubes in acidic solution exhibit 10 times higher specific activity than octahedral Pd nanoparticles which have predominantly Pd(111) facets on the surface [15]. Liu and co-workers tested 27, 48 and 63 nm Pd cubes for ORR and from these 48 nm nanocubes were found to be the most active. The activity surpassed that of 9 nm spherical Pd nanoparticles and was suggested to be due to decreased OH⁻ adsorption [11]. However, Huang et al. showed that the kinetic current density of the ORR on Pd nanocubes was rather similar in 0.1 M and 1 M NaOH solutions [14]. Recently, Liu et al. demonstrated the influence of supporting material of Pd nanocubes on the ORR in alkaline solution [16]. It was found that the reduced graphene oxide nanosheets improve the ORR onset potential of the catalyst.

In this study three different size carbon-supported Pd nanocubes were prepared and their activity towards the ORR in alkaline solution was tested to find out if changing the particle size or metal loading on carbon has an effect on the electrocatalytic activity of the catalysts. In acid media the carbon-supported Pd nanocubes had higher specific activity than spherical Pd nanoparticles and commercial Pd/C catalyst [17] and therefore the purpose of the present research was to compare the ORR activity trends in 0.1 M KOH.

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2. Experimental

Pd nanocubes were prepared by methods described previously using ascorbic acid as reducing agent and cetyltrimethylammonium bromide or polyvinylpyrrolidone as capping agent [18–20]. After the synthesis, Vulcan XC72 (Cabot) carbon was added to form 20 wt% and 50 wt% Pd/C catalyst. The samples were cleaned by adding NaOH pellets to the suspension, filtered and washed several times with water [21]. Finally the catalysts were dried overnight at 75 °C. The catalysts are designated as PdCub1–20, PdCub1–50, PdCub2–20 and PdCub3–20, where PdCub1, PdCub2 and PdCub3 correspond to Pd nanoparticle size of 30, 10 and 7 nm, respectively and 20 or 50 indicate Pd loading on carbon. For comparison purposes, carbon-supported spherical Pd nanoparticles were prepared (PdSph–20) [9,22] and commercial Pd/C catalyst (20 wt% Premetek Co, USA) was also tested.

The catalyst ink (1 mg ml^{-1}) was prepared by mixing the catalyst powder in water containing 0.5% of Nafion (Aldrich) and pipetted onto the glassy carbon (GC) electrode (5 mm in diam.) to have the Pd/C catalyst loading of 0.1 mg cm^{-2} . The electrochemical measurements were carried out in 0.1 M KOH solution, which was saturated with Ar (99.999%, AGA) or O_2 (99.999%, AGA). The solution was made from KOH pellets (puriss p.a., Sigma-Aldrich) and Milli-Q water. The electrochemical measurements were carried out in three-electrode glass cell with reversible hydrogen electrode (RHE) as reference (all potentials are given with respect to RHE) and a Pt wire separated by a glass frit served as a counter electrode. An EDI101 rotator with CTV101 speed control unit (Radiometer) was used for rotating disk electrode (RDE) experiments. The potential was applied with Autolab PGSTAT30 potentiostat/galvanostat (Metrohm Autolab). The experiments of CO stripping, cyclic voltammetry (CV) and oxygen reduction were carried out similarly to previous publications [9,10,17]. The experiments were repeated five times for better evaluation of the catalysts.

For transmission electron microscopy (TEM) images JEM-2010 (JEOL) instrument was used. The accelerating voltage was 200 kV.

The thermogravimetric analysis (TGA) was carried out using a Mettler-Toledo TGA/SDTA851 thermobalance with a temperature ramp of 10 °C min^{-1} from 25 to 850 °C in an oxidative atmosphere ($\text{N}_2:\text{O}_2 = 4:1$).

3. Results and discussion

3.1. Physical characterisation of Pd/C catalysts

The representative TEM images of carbon-supported Pd nanocubes are presented in Fig. 1. As expected, the majority of the particles are cubic and the particle size depends on the synthesis method employed, being about 30 nm for PdCub1, 10 nm for PdCub2 and 7 nm for PdCub3. Based on previous studies it is safe to assume that the Pd(100) crystal facet prevails on the surface of these nanocubes [10,22].

The real Pd content in the catalysts determined by thermogravimetric analysis was in good agreement with the expected values: PdCub1–20 contained 18 wt%, PdCub1–50 49 wt%, PdCub2–20 18 wt% and PdCub3–20 19 wt% of Pd.

3.2. CO stripping and CV studies

First the studied electrodes were subjected to oxidation of pre-adsorbed CO, in order to clean and characterise the surface. Fig. 2a shows that initially the whole surface is blocked with CO, which is oxidised completely during one potential cycle up to 1 V, resulting an oxidation peak at ca. 0.8 V. After the CO stripping experiments potential was cycled between 0.1 and 0.8 V for additional cleaning and characterisation. After the ORR measurements the CV curves were registered between 0.1 and 1.4 V (Fig. 2b) in order to calculate the electroactive

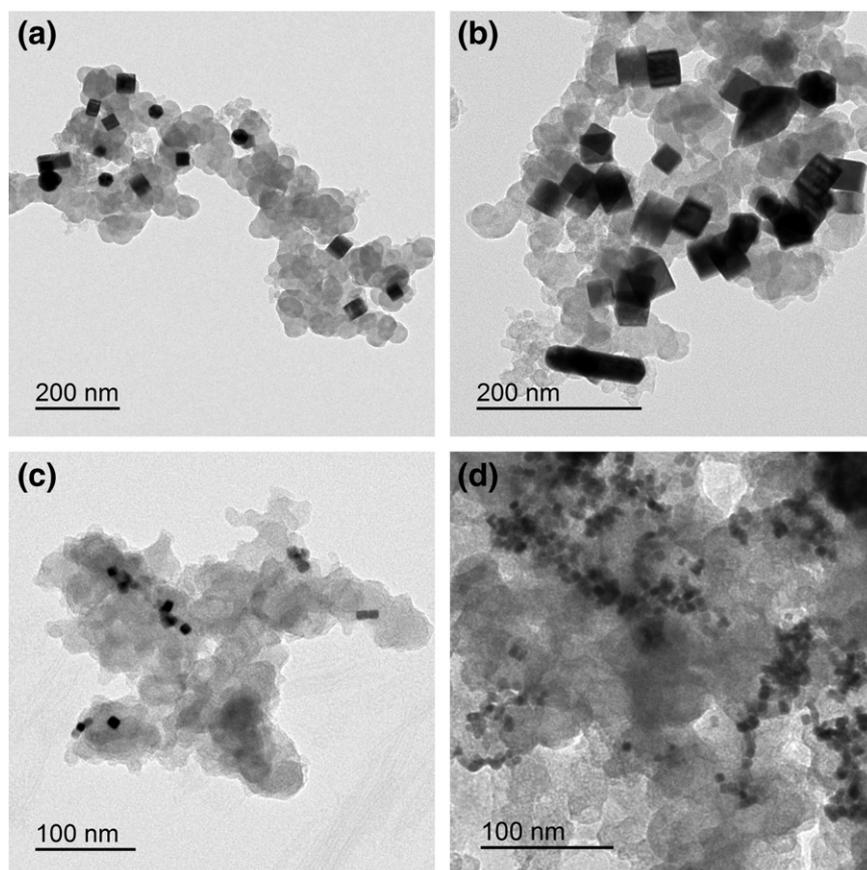


Fig. 1. TEM images of carbon-supported Pd nanocubes (a) PdCub1–20, (b) PdCub1–50, (c) PdCub2–20 and (d) PdCub3–20.

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