Accepted Manuscript

Recent progress in oxygen reduction electrocatalysis on Pd-based catalysts

Heiki Erikson, Ave Sarapuu, Jose Solla-Gullón, Kaido Tammeveski

PII: S1572-6657(16)30492-1
DOI: doi: 10.1016/j.jelechem.2016.09.034
Reference: JEAC 2848

To appear in: *Journal of Electroanalytical Chemistry*

Received date: 15 July 2016
Revised date: 20 September 2016
Accepted date: 21 September 2016

Please cite this article as: Heiki Erikson, Ave Sarapuu, Jose Solla-Gullón, Kaido Tammeveski, Recent progress in oxygen reduction electrocatalysis on Pd-based catalysts, *Journal of Electroanalytical Chemistry* (2016), doi: 10.1016/j.jelechem.2016.09.034

Recent progress in oxygen reduction electrocatalysis on Pd-based catalysts

Heiki Erikson[a], Ave Sarapuu[a], Jose Solla-Gullón[b], Kaido Tammeveski[a,*]

[a]*Institute of Chemistry, University of Tartu, Ravila 14a, 50411 Tartu, Estonia*

[b]*Instituto de Electroquímica, Universidad de Alicante, Apartado 99, 03080 Alicante, Spain*

Abstract

Palladium-based catalysts for electrochemical reduction of oxygen have received increasing attention as potential replacement for platinum-based materials in the fuel cells. This Review summarises the research conducted with nanostructured palladium catalysts, including thin nanostructured films and Pd nanoparticles on various carbon and non-carbon supports. The mechanism of oxygen reduction on palladium is described and the effect of the particle size and shape on the electrocatalytic activity is emphasised. The role of the support material and additives on the oxygen reduction activity of Pd nanoparticles is also discussed. The electrocatalytic activity of Pd-based catalysts is evaluated in terms of specific activity and mass activity. The application of supported Pd nanoparticles as cathode catalysts for low-temperature fuel cells is highlighted. Some insights into the remaining challenges and directions for further development of Pd-based oxygen reduction electrocatalysts are provided.

Keywords: Oxygen reduction reaction, Pd nanoparticles, Pd nanocubes, Pd-based catalysts, Pd films, Pd single crystals, Composite catalysts, Electrocatalysis

1. Introduction

In the development of polymer electrolyte fuel cells palladium has gained much attention as a possible cathode catalyst in the recent years. Palladium is in the same group with platinum, which is the most active metal catalyst for oxygen reduction reaction (ORR) and they have similar chemical and physical properties. Palladium nanoparticles (PdNPs) can be prepared using several methods, in order to design advanced cathode catalysts for ORR in fuel cells. Various support materials have been employed for PdNPs to improve their utilisation. Nanostructured Pd electrodes have been used to further elucidate the tendencies of electrocatalytic behaviour towards the ORR. Alloying has a large influence on the ORR

---

[*] Corresponding author. Tel.: +372-7375168; fax: +372-7375181
E-mail address: kaido.tammeveski@ut.ee (K. Tammeveski)

activity of Pd-based catalysts, but these effects are outside the scope of this review and may be further read elsewhere [1].

This review focuses on the results of the electrocatalytic oxygen reduction reaction on Pd-based catalyst materials. Particle size, substrate effects and crystallographic effects are discussed. PdNP-based composite materials will be also dealt with as electrocatalysts for ORR.

2. ORR on bulk polycrystalline and single-crystal Pd electrodes

The ORR and its kinetics on palladium electrodes in aqueous solutions has been thoroughly studied [2-5]. The early work by Tarasevich [4] and Vracar et al. [2, 3] on bulk Pd electrodes showed that E-log i_k relationships have two distinct regions, at low current densities the Tafel slope value being close to –60 mV and at high current densities close to –120 mV. Kinetic expressions have been derived, which describe reasonably well these experimental tendencies [2, 3]. It was determined that the reaction order with respect to molecular oxygen is one in both current density regions in acid and alkaline solutions [4] and the rate-determining step for ORR is the slow transfer of the first electron to oxygen molecule [2]. Further studies have revealed that the Tafel slope of –60 mV corresponds to the surface that is covered by oxygen-containing species and the change in the slope arises from the differences in the adsorbed oxygen coverage [3]. Adsorbed oxygen has been suggested to inhibit the ORR kinetics [4]. More recently it has been determined that on the polycrystalline Pd electrodes the ORR in alkaline and in acid media proceeds mainly via four-electron pathway producing water in the potential range where Pd is oxide free or oxidised to PdOH, while a two-electron pathway prevails in the potential region where PdO is on the surface [5].

The oxygen reduction reaction on palladium is structure sensitive. Hoshi and co-workers have studied the ORR on low and high index planes of palladium in perchloric acid (Figure 1) [6]. It was determined that the reduction current density at 0.90 V vs RHE is increasing in the following order on the low index planes: Pd(110) < Pd(111) < Pd(100), which is opposite to that of platinum in the same solution [6]. The kinetic current normalised to electroactive surface area (specific activity, SA) of Pd(100) was observed to be about three times higher than that of the most active single crystal facet of Pt. On all Pd single-crystal facets the ORR proceeds via 4-electron reduction pathway, analogously to that on Pt. The conclusion that Pd(100) is the most active single crystal facet of Pd for ORR was supported by studies on high index facets [6]. The current densities at 0.9 V vs RHE on n(100)-(111) series depended linearly on the terrace atom density, showing that the active site for the ORR on Pd electrodes is the terrace [7], whereas on Pt it is the step. Thus it has been suggested that the reaction mechanism on Pd may differ from that on Pt electrodes. The activities of low-index crystal facets may be different in sulphuric acid and in alkaline solution as these anions have different adsorption energies, but unfortunately there has been no studies of Pd(*hkl*) neither in sulphuric acid nor in alkaline solution.

3. ORR on nanostructured Pd films

Nanostructured metal films can be prepared by various techniques, such as electrodeposition [8-13], vacuum evaporation [14-16] or magnetron sputtering [17]. The structure of the thin films can be easily tuned, which allows studying the effect of surface morphology on the electrocatalytic properties of metal catalysts.

Vacuum-evaporated thin Pd films consisting of Pd nanoislands have been used as model electrodes to study the particle size effects, as the island size increases with the film thickness. Pd films with nominal thickness of 0.25–10 nm were evaporated onto Au and glassy carbon (GC) substrate and the ORR kinetics has been studied in acidic and alkaline solutions (Figure 2) [14, 15]. In perchloric acid and in potassium hydroxide solutions the ORR specific activity did not depend on the Pd film thickness or size of Pd nanoislands, but in sulphuric acid it increased with increasing the film thickness. This was attributed to the strong adsorption of (bi)sulphate anions which block the active sites for oxygen adsorption [14, 15].

The morphology of oxide-derived Pd films on Ti substrate has shown to be similar to that of bulk Pd [18]. The ORR proceeds at least partially via two-electron pathway on this material in alkaline solution and is a first order reaction in respect to O_2.

On Pd islands electrodeposited onto highly oriented pyrolytic graphite (HOPG) at different conditions the ORR in perchloric acid solution significantly depended on the structure of the material [8]. The changes in the activity were attributed to different crystallographic structure and particle size. The main increase in activity was suggested to arise from the edges of the islands, where the substrate influences the electronic structure of Pd particles and weakens the O-O bond. Comparing the ORR on PdNPs deposited onto nitrogen-doped and undoped HOPG supports it has been revealed that doping of HOPG does not affect the SA on PdNPs [9, 16]. Reduced stability of Pd on N-doped HOPG was observed, which was attributed to interactions between nitrogen-containing groups and Pd [9].

For electrodeposited Pd on glassy carbon in sulphuric acid solution as well in potassium hydroxide, the specific activities of ORR and Tafel slope values were comparable to those of bulk Pd, but the value of *n* was lower than 4, indicating peroxide formation [10]. On Pd electrodeposited onto gold substrate, the ORR behaviour was similar to that on Pd/GC in sulphuric acid, but enhanced specific activities were obtained in alkaline solution, which were suggested to be due to substrate effect [11]. PdNPs electrochemically deposited onto oxygen-terminated boron-doped diamond electrodes have shown good electrocatalytic activity towards the ORR in alkaline solution, in which the ORR proceeds via 4-electron reduction pathway [12]. Thin films that are electrodeposited from protonic ionic liquid onto glassy carbon had higher electroactive surface area and electrocatalytic activity than those deposited from aprotic liquid or from aqueous solution under similar conditions [13]. Kang et al. demonstrated that dendritic Pd structures prepared by electrodeposition have higher electrocatalytic activity than that of commercial Pt/C [19].

4. ORR on carbon-supported Pd catalysts

For practical applications as catalysts, PdNPs are supported onto various materials. Carbon black is the most common support material, thanks to its high surface area, good conductivity and affordable price. However, new materials with superior performance, such as carbon nanotubes (CNTs), graphene etc., have emerged during the last decades. The structure of the support material can influence the performance of the catalysts in various ways. For instance, it determines the degree of agglomeration of nanoparticles, may change intrinsic activity of supported metal via electronic effects and controls the efficiency of the mass transport in the fuel cell. In addition, the stability of a catalyst is greatly influenced by the corrosion resistance of carbon support.

4.1. *ORR on Pd/C* catalysts

Palladium nanoparticles can be supported on different carbon blacks and the activity of these catalysts depends on the preparation method. For instance, it has been shown that the activity of Pd/C can be improved by pre-treatment of carbon support [20]. Variations of the properties of the support material yielded Pd nanoparticles of different size, degree of agglomeration and electrocatalytic activity. The changes in the ORR activity were attributed to interactions between carbon support and Pd particles, but also to different distribution of particles on support. The four-electron pathway of ORR was reported on all Pd/C catalysts studied, independently of the carbon support [20]. However, Pd/C catalysts which were prepared by using different carbon blacks showed similar ORR activity, but the stability of the catalysts varied noticeably [21].

Alvarez et al. prepared Pd/C catalysts using different reducing agents and demonstrated that the ORR on these catalysts has similar reaction mechanism, but the specific activity varies greatly due to different morphologies (Figure 3) [22]. The decrease of mass activity of Pd/C in sulphuric acid as a result of the heat-treatment of the catalyst was attributed to increasing the size of PdNPs [22]. The distribution of Pd nanoparticles on carbon support can be improved by modifying the traditional sodium borohydride reduction method by introducing ammonia [23].

Using carbonyl chemical route in the preparation of carbon-supported PdNPs with various metal loading resulted in catalysts with diverse morphologies and variable electrocatalytic activity [24]. These materials showed similar Tafel slope (–60 mV) at low current densities in perchloric acid solution, but the slope varied in alkaline solution.

Palladium nanoparticles supported on carbon paper have shown high electrocatalytic activity in sulphuric acid solution, which has been attributed to the favourable structure of the catalyst consisting of small Pd particles that are connected through grain boundaries [25]. In further work it was revealed that the performance of this catalyst in membrane electrode assembly (MEA) at high current densities was better than that of Pt black, which was suggested to be due to the differences in metal distribution [26]. Unfortunately the severe reduction of the catalyst loading in the cathode led to the decrease in the fuel cell performance. The activity of PdNPs on carbon paper was further improved by employing potentiostatic electrodeposition instead of electroless deposition, resulting in particles with cubic, triangular and plate-like structures that may contribute for better utilisation of the catalyst [27].

Testing of carbon-supported palladium oxide-based catalysts has shown that PdO itself is rather inactive towards the ORR in perchloric acid, but the activity increases when the oxides are reduced [28]. In addition, on oxide covered Pd electrode the peroxide yield is higher than on oxide-free surface as a result of active site blocking by the oxides. The same conclusion was reached also in alkaline solution [29]. It has been suggested that the preparation of Pd catalyst by hydrated palladium oxide route leads to a lower generation of peroxide during the ORR process [30]. Interactions between Pd and palladium oxide might be the reason of this observation, as oxide may inhibit the peroxide pathway or it may alternatively catalyse the decomposition of the formed H_2O_2 [30].

Lower hydrogen peroxide yields on Pd/C as compared to Pt/C have been observed at working fuel cell potentials in alkaline solution [31]. This variation has been explained by different activation energies for O-O bond breaking. At the same time an advantage of Pd/C was shown to have lower sensitivity to ethanol compared to Pt catalyst.

4.2. *ORR on Pd/CNT catalysts*

Carbon nanotubes as electrocatalyst support have many advantageous properties, such as large surface area, good conductivity, high stability and suitable porous structure. PdNPs deposited onto carbon nanotubes and nanofibers have been employed as active catalysts for ORR [32-38]. The ORR has been suggested to follow two-step two-electron transfer pathway on PdNP/CNTs [34] and also on PdNPs supported on polymer-modified CNTs [39]. PdNPs supported on carbon nanofibers have displayed higher electrocatalytic activity than those on amorphous carbon support [40]. However, it has been found that palladium electrodeposited onto carbon nanotubes is less stable than that on Vulcan XC-72 carbon, but on both substrates the ORR activity decreases due to a gradual agglomeration of Pd particles [41].

Palladium nanoparticles supported on multi-walled carbon nanotubes have shown a relatively large degree of agglomeration [42]. Despite agglomeration the ORR proceeded via 4-electron pathway and the SA surpassed that of bulk Pd two times in 0.5 M H_2SO_4 and three times in 0.1 M KOH. In order to improve the nanoparticle distribution, Wang et al. suggested to modify CNTs with heteropolyacids and poly(diallyldimethylammonium chloride) (PDDA) [43]. They were able to obtain homogeneous distribution of PdNPs on functionalised nanotubes that resulted in higher ORR activity of the catalyst as compared to strongly agglomerated PdNPs on clean acid-treated CNTs. Similarly, modification of CNTs with phosphotungstic acid and PDDA has been shown to enhance the distribution of PdNPs; in addition, the synergistic effect of phosphotungstic acid was suggested to improve the ORR activity [44].

Jukk et al. studied ORR on multi-walled carbon nanotubes decorated with sputter-deposited Pd nanolayers with nominal Pd thicknesses of 5, 10 and 15 nm [45]. The specific activity in sulphuric acid solution was reported to be lower than that of bulk Pd for all electrodes, but in alkaline solution the SA of Pd/MWCNT catalysts with thicker Pd layers surpassed that of bulk Pd. It was suggested that favourable crystallographic structure is the cause for increased activity in alkaline media and the adsorption of (bi)sulphate decreases the activity in sulphuric acid. As a continuation the heat-treatment effect on Pd/MWCNT composites in alkaline solution was studied, which revealed that increasing annealing temperature from 300 to 500 °C improved the specific activity towards the ORR [46]. It was suggested that annealing increases the fraction of Pd(100) surface sites that have been determined to have the highest ORR activity in perchloric acid solution [6]. Carbon nanotubes on carbon paper has proven to be a beneficial support for sputter-deposited Pd used as a cathode in an anion exchange membrane fuel cell, enabling high performance at ultra-low loading, thanks to high Pd utilisation [47].

SiO_2-covered Pd/CNTs have been shown to be initially rather inactive in comparison to Pd/CNT, but the activity improved during potential cycling and remained only slightly lower than that of clean Pd/CNT, while the activity of Pd/CNTs decreased during electrochemical testing [48, 49]. It was proposed that silica layers work as diffusion barrier for oxygen, protons and water molecules and also for peroxide, which is reduced to water when it forms.

Porphyrins have also been used to modify nanotubes and the resulting composite catalyst with PdNPs has shown good activity for the ORR [50].

4.3. *ORR on Pd/graphene catalysts*

Graphene has gained much attention in recent years and, due to its unique electronic properties and large surface area [51], it has also been utilised as a support material for metal-based catalysts [52-59]. Graphene sheets as support material facilitate the dispersion of PdNPs and the resulting materials show enhanced ionic diffusion and charge transfer [54, 55]. Kakaei and Gharibi demonstrated that depositing Pd onto graphene/carbon paper yields better dispersion, lower charge transfer resistance and higher electroactive surface area than on pure carbon paper [56].

The benefit of reduced graphene oxide (rGO) support has also been suggested to be originated from the interactions between Pd and graphene that cause strain in Pd structure due to electron exchange [60]. PdNPs on graphene quantum dots exhibit good ORR activity, which is attributed to optimal concentration of defects in the support that provide sufficient electron withdrawal from the Pd particles [61]. Likewise, Pd nanocubes supported on graphene nanosheets with high number of physical defects showed higher activity and stability as compared to similar nanocubes deposited on graphene nanosheets with higher number of oxygen containing functional groups [62].

Using rGO as a support material has improved the ORR activity of Pd catalyst over conventional carbon black support in sulphuric acid solution; interestingly, no improvement was observed on Pt catalyst [63]. Pd nanoparticles deposited onto graphene sheets have shown higher ORR activity in alkaline media at high metal loadings than similar Pt catalyst (Figure 4) [52]. Graphene supported PdNPs had higher electrocatalytic activity than Pd alloys in alkaline solution, but in sulphuric acid alloys with Co and Fe were more active than Pd/rGO [53].

Additional improvement of the performance of graphene-supported Pd catalysts can be achieved by modifying the graphene surface. For instance, Kim et al. have proposed that using linker molecules between graphene and PdNPs enables better dispersion of graphene sheets and facilitates distribution of Pd and Pt nanoparticles, whereas longer hydrocarbon chains in the linker were found to be more beneficial for ORR than shorter ones [57]. Using poly(3,4-ethylenedioxythiophene) functionalised graphene as support material has yielded Pd catalyst displaying higher specific and mass activity than Pt/C and Pd/rGO, which was explained by synergetic effect [58].

4.4. ***ORR on PdNPs supported on N-doped carbon materials***

Nitrogen-doped carbon materials have found wide application in the design of metal nanoparticle based catalysts. Nitrogen doping remarkably changes the properties of the carbon substrate, thereby affecting the electrocatalytic performance of metal nanoparticles [64]. For example, in sulphuric acid both Pd and Pt catalysts have shown enhanced ORR activity on N-doped carbon as compared to undoped carbons [65]. PdNPs supported on nitrogen-doped graphene (NG) nanosheets have shown twice as high specific activity than bulk Pd, which has been attributed to small particle size, uniform dispersion of PdNPs and strong adhesion between carbon and metal [66]. Strong binding between PdNPs and NG is suggested to prevent the agglomeration of nanoparticles and thus improve the stability [67]. However, no benefit of nitrogen doping on HOPG has been observed [16]. This is surprising result, since for most heteroatom-doped carbon supported Pd catalysts an enhanced electrocatalytic activity was observed. Apparently this is related to special features of N-doped HOPG used in that particular work.

Ye et al. prepared and tested PdNPs on nitrogen-doped ordered mesoporous graphitic carbon nanospheres in alkaline medium (Figure 5) [68]. Pd was strongly bound to this material and high amount of quaternary-N is believed to be beneficial for the ORR kinetics. Simultaneous N-doping, carbon graphitisation and Pd^{2+} reduction is suggested to promote strong coupling of palladium and nitrogen, thereby improving the ORR activity and stability of the catalyst [68].

Carbon supports of different morphology and surface composition can be synthesised by pyrolysing microporous organic polymers, which retain porosity and high surface area [69, 70]. Pd nanoparticles prepared on this support exhibit high electrocatalytic activity for ORR, which was attributed to nitrogen heteroatom-induced altering of the electronic structure and high stability. Graphitic carbon nitride (g-C_3N_4) prepared by rapid combustion method has shown to be suitable substrate for PdNPs [71]. This composite material had high electrocatalytic activity and stability in alkaline solution, which was attributed to synergistic charge-transfer effect between Pd and g-C_3N_4, suitable porosity of the catalyst and uniform distribution of PdNPs. High stability of similar catalysts in perchloric acid solution has also been demonstrated, which is suggested to be the result of changing the electronic structure of Pd due to synergistic effect [72].

Recently, Compton and co-workers have proposed an elegant approach for evaluating the ORR kinetics on N-doped carbon nanotube-supported Pd catalysts [73]. It was suggested on the basis of the results obtained on single nanoparticle catalysts and theoretical modelling that the ORR on Pd involves the initial formation of $O_2^{\bullet-}$ in sulphuric acid solution.

5. The effect of additives on the ORR on PdNPs

Different additives can increase or decrease the electrocatalytic activity of palladium nanoparticles towards the ORR. Amorphous palladium particles containing phosphorus have been synthesised by using sodium hypophosphite as a reducing agent [74]. Specific and mass activities for these particles were reported to be over 4.5 and 2.6 times higher, respectively, than those for Pd and Pt catalysts. X-ray diffraction patterns indicate that this catalyst can be regarded as an alloy in which the crystal structure is significantly changed as compared to pure Pd. On the contrary, dissolved carbon in Pd lattice decreased the ORR activity of PdNPs as compared to bulk Pd and pure PdNPs [75].

The positive effect of organic polymers on the ORR activity of Pd nanoparticles has also been observed [76-80]. Pd on polypyrrole (PPy) mixed with carbon powder have higher ORR activity as compared to Pd/C [76]. The ratio of PPy-to-Pd plays a decisive role in the electrocatalytic performance of PdNPs on polypyrrole [77]. The optimal Pd content was 10-12%, at which the ORR proceeded mainly via 4-electron pathway, and with increasing Pd content the peroxide production also increased. Pd icosahedra functionalised with polyallylamine have displayed 4.5 times higher specific activity than that of commercial Pt black [78]. PdNPs functionalised with oleylamine show not only enhanced electrocatalytic activity towards the ORR, but are also tolerant to formic acid due to steric blocking [79]. Similarly PdNPs supported on polydiallyldimethylammonium chloride-functionalised carbon black have shown higher ORR activity and stability than commercial Pd/C [80]. The enhanced ORR activity has been suggested to be due to nitrogen groups in these ligands that interact with Pd nanoparticles by changing their electronic structure [78]. Nafion is used as a binder for the ORR measurements and in fuel cell as proton exchange membrane, but it has been demonstrated that it increases the peroxide production on PdNPs [81]. Pd nanoclusters with a mass of approximately 5 kDa have been used to show that thiolate on Pd particles causes negative shift of ORR onset potential [82]. While protected nanoparticles have better stability in air, the cleaned Pd nanoclusters have higher mass activity surpassing that of Pt/C.

The compounds used in the synthesis of Pd nanoparticles can also decrease the ORR activity and thus the removal of these supplements is very important [83, 84]. Frequently heat-treatment or thorough washing and centrifugation are used for cleaning, but chemical approach can also be employed. A comparison between using tert-butylamine (TBA) and heat-treatment showed that the chemical route is more efficient in removing Br^- and polyvinylpyrrolidone (PVP) [83]. However, TBA is not effective for all capping agents and stabilizer compositions, for example for removal of citric acid and PVP [84]. More efficient removal of the capping agents and stabilizers can be achieved by treatment with $NaBH_4$, which can remove ~90% of the impurities and the rest 10% is shown not to have an effect on the electrocatalytic behaviour towards the ORR [84].

6. ORR on Pd catalysts supported on oxides and carbides

Pd nanoparticles have been also supported on various non-carbon materials, such as oxides [85-96] and carbides [97, 98]. The main advantage of these materials is their high stability, but the application of these catalyst supports is hindered by their low electrical conductivity [99]. This can be overcome by addition of carbon nanomaterials.

Oxygen reduction on Pd nanoparticles supported on zeolite 13X follows $4e^-$ pathway in alkaline solution and the electrocatalytic activity of this material can be further increased by adding carbon powder, which increases the electrical conductivity and porosity of the electrocatalyst [85].

Pd on titanium suboxides have shown to catalyse a two-electron pathway of ORR, while the stability of this support material was observed to be superior to carbon black-based catalysts [86]. PdNPs on carbon support modified with different ratios of TiO_2 (anatase) have proven to be better catalysts for ORR than pure Pd/C in perchloric acid [87]. TiO_2 may change the interactions between Pd and water and possibly oxygen [88] or change the coverage of the oxidised species on the surface [87] and as a result the activity of the composite catalyst increases as compared to Pd/C [87, 88].

In alkaline solution MnO_2 has shown to improve the activity of PdNPs and the mass activity of Pd@MnO_2/C has been found to surpass that of Pd/C about 2.5 times [89]. Mn_2O_3-supported Pd possesses ORR activity comparable to that of commercial Pt/C catalyst, which is suggested to be due to mesoporous structure and the synergetic effects between supporting Mn_2O_3 and Pd [90]. The synergetic effect of Mn has been used to explain the enhanced ORR activity of PdO/C catalysts synthesised using Mn_3O_4/C and $PdCl_2$ as precursors [91]. However, it has also been proposed that higher activity of Pd-Mn_3O_4 catalysts as compared to that of Pd/C is not the result of the interactions between Pd and transition metal oxide, but due to the facilitated oxygen transport to palladium [92]. Another option is to use mixed valence oxide in combination with graphene nanosheets as a support material for PdNPs; from these, $MnCo_2O_4$/graphene support has shown better results than $CoCo_2O_4$/graphene and $NiCo_2O_4$/graphene and comparable activity to a Pt/C catalyst [93].

Increased ORR activity of Pd has been observed also on WO_3/C support, but SnO_2/C did not show improvement over pure Pd/C [94]. The metal oxides were suggested to decrease the oxygen adsorption strength and thus increase the activity for ORR. The superior ORR activity of Pd-WO_3/C has also been attributed to small particle size, good dispersion of PdNPs on support material, interactions between Pd and WO_3 and also to the possible formation of hydrogen tungsten bronze (H_xWO_3) [95]. The activity of Pd/SnO_2-C has been increased by heat treatment [96].

PdNPs on reduced polyoxometalates (rPOM) exhibit better ORR activity and stability in alkaline solution than commercial Pd/C and Pt/C as a result of electron delocalisation between Pd and rPOM [100]. While Pd/C had a positive shift in Pd 3d binding energy during the stability tests, for the Pd/rPOM catalyst it remained unchanged, suggesting lower aggregation due to better interaction between Pd and rPOM.

Likewise, enhanced ORR activity of Pd by metallic carbides has been observed. Composites of Pd, graphitic carbon and carbides (Fe_2MoC [97], MoC [97] and Co_3W_3C [98]) have shown higher activity as compared to Pd/C and Pt/C catalysts, which was attributed to electron donation from carbides to metallic Pd, whereas stronger interactions between the carbides and Pd contribute to the higher stability [97, 98].

Thus, the support material may have a major contribution to the electrocatalytic behaviour of the catalyst and the increase of the ORR activity is most likely due to the interactions between Pd and oxide, which affect the electronic structure.

7. Effect of Pd particle size on the ORR activity

Determining the effect of Pd particle size on the activity of the oxygen reduction reaction is an important task in order to prepare electrocatalytically active and economically beneficial

Pd-based catalysts. Jiang et al. studied particle size effect on carbon-supported Pd catalysts in alkaline solution (Figure 6) [101]. Increasing the particle size from 3 to 16.7 nm resulted in a threefold increase of the specific activity. The lower SA of smaller particles was suggested to be due to the adsorbed OH^- ions that block the active sites. The mass activity showed the maximum value at 5 nm, which can therefore be regarded as the optimal value of particle size for fuel cell applications [101].

The values of mass activity and specific activity of oxygen reduction on Pd/C have been reported to rise up to average Pd particle of 11 nm in perchloric acid solution [102]. In contrast, Zhou et al. observed increasing mass activity with decreasing the particle size, whereas specific activity was found to have the largest value between 5 and 6 nm [103]. The particle size effect was attributed to a concurrence of several factors like distribution of low index planes on the surface, the number of low coordination sites and the electronic structure of Pd. More recently, Ju et al. studied the Pd particle size effect in H_2SO_4 solution on Pd electrodeposited onto highly oriented pyrolytic graphite (HOPG) [104]. Increase of the activity of the electrodes with Pd particle size was observed and particles larger than 10 nm behaved similarly to bulk Pd [104]. Lower activity of smaller particles was primarily attributed to the higher ratio of low-coordinated surface atoms.

Recently Antolini has thoroughly reviewed the particle size effect and described its background for fuel cell catalysts [105]. It was summarised that the main causes for particle size effect are structural sensitivity i.e. dependence of the surface geometry, electronic state of the catalyst, the potential of zero total charge and metal-support interactions.

8. Effect of Pd particle shape on the ORR activity

As different single-crystal facets present different electrocatalytic activities [6], the ORR has been studied on shape-controlled Pd nanoparticles. As already noted the most active single crystal facet of Pd is (100) [6] and thus, the most active Pd particles should be cubic in shape [106]. The ORR studies on carbon-supported Pd nanocubes in perchloric acid have shown that these were 10 times more active in $HClO_4$ than spherical and octahedral particles, which was attributed to higher onset potential of OH_{ad} formation [107, 108]. In H_2SO_4 solution, the SA on Pd nanocubes was 17 times higher than that of the octahedra, possibly due to the stronger adsorption of (bi)sulphate anions on Pd(111) surface sites [108]. The unsupported Pd nanocubes showed three times higher SA than those of spherical PdNPs and bulk Pd in sulphuric acid [109] and in alkaline solution the SA of cubic PdNPs was 4 times higher than that of spherical PdNPs (Figure 7) [110]. As noted by Hoshi and co-workers, the reaction mechanism on Pd may differ from that on Pt [6] and the Tafel slope value at high current densities has been reported to be higher than -120 mV [110]. The SA of carbon-supported Pd nanocubes with the side length of 7, 10 and 30 nm was at least two times higher than that of commercial Pd/C and spherical Pd/C and increased with the nanocube size [111, 112]. The mass activities increased with decreasing the size of the nanocubes, whereas the mass activity of 7 nm nanocubes was comparable to that of commercial Pd/C catalysts. These observations are in agreement with the results reported by Jiang et al. [101]. Pd nanocubes with sizes of 27, 48 and 63 nm showed different specific activities in alkaline solution, with 48 nm Pd nanocubes having the highest SA, which was suggested to be due to the significant suppression of the OH^- adsorption on smaller Pd cubes [113]. Similarly, 48 nm Pd nanocubes were the most active in sulphuric acid, which was explained by different adsorption strengths of (bi)sulphate ions [114]. It was also found that Pd nanocubes have smaller sensitivity for methanol addition than spherical PdNPs [114]. Results reported by Arjona et al. give further support that the electrocatalytic activity of Pd nanocubes for ORR in alkaline solution is higher than that of commercial Pd/C catalysts [115]. The SA values of truncated Pd nanocubes were higher than those of traditional Pd nanoparticles and did not depend on hydroxide concentration [116]. Even though the differences in OH^- adsorption were in evidence on the CVs registered in O_2-free 0.1 M and 1 M NaOH, the Tafel slope value and thus the reaction mechanism was the same in both solutions. The mass activities of Pd nanocubes supported on graphene nanosheets surpassed that of commercial Pt/C and Pd/C more than 2.6 times [62].

In contrast, Shao et al. did not observe any structure dependence for ORR on small PdNPs (5−6 nm) of different shape in alkaline solution [108]. They proposed that both inner-sphere and outer-sphere electron transfer mechanisms are possible in alkaline media and the latter dominates in the potential region of Pd oxide formation. Also the adsorption energies of O_2 and oxygen-containing intermediates on catalyst surface may affect the ORR [108, 117]. Triangular Pd nanorods having mainly (111) facets and partially (100) facets on the surface were prepared by electrodeposition and it was found that the latter contributes the most to the reported electrocatalytic activity towards the ORR [118]. Pd nanocubes supported on multiwalled carbon nanotubes have been employed as a cathode catalyst in hybrid biofuel cell as the nanocubes showed good stability and activity in wide pH range [119].

Pd nanorods with predominant (110) surface facet showed superior ORR activity in perchloric acid solution as compared to Pd nanoparticles and comparable activity to bulk Pt [120]. According to the results of the density functional theory (DFT) calculations, this can be explained by decreasing the adsorption energy of O adatoms on Pd single crystals, which follows the sequence of Pd(100) > Pd(111) > Pd(110) [120]. It was suggested that lower adsorption energy results in a higher ORR activity, but this contradicts the ORR activity series reported by Kondo et al. [6].

Bromide treatment has been employed to increase the amount of (111) facets on Pd nanoparticles [121]. The Br-treated particles showed increase in ORR activity in perchloric acid solution and enhanced stability. Pd nanoflowers prepared via electrodeposition in the presence of polyethylene glycol had predominant Pd(111) surface facets and displayed enhanced ORR activity in H_2SO_4 solution as compared to Pd/C, which was attributed to improved electrochemical surface area [122].

Sacrificial templates can also be used to prepare Pd catalysts with predefined shape. Poly(ethylene oxide) fiber mats have been used as template for magnetron sputtering of Pd catalyst onto the HOPG surface, resulting in three-dimensional Pd shells [17]. Thanks to their higher electroactive surface area, these structures had higher electrocatalytic activity than Pd films prepared without the template. Copper adlayers have been used as sacrificial template in which initial metal is replaced by another (Pt, Pd, Ag) via galvanic replacement reaction [123]. Pd nanoshells [124] and nanotubes [125] prepared using his methodology show comparable ORR activity to commercial Pd and Pt catalysts, which was attributed to the enhanced surface area and high porosity of these materials.

The stability of Pd based catalysts is a major issue. Several reports show enhanced activity of Pd nanocubes enclosed with Pd(100) facets for alkaline ORR [110, 113, 115]. However, Zadick et al. have shown that Pd nanocubes lose their shape when cycled in alkaline solution in the potential range from 0 to 0.9 V vs RHE, where both H_{UPD} and Pd surface oxidation takes place [126]. When potential window is limited to only surface oxidation (from 0.4 to 0.9 V vs RHE) or H_{UPD} region (from 0 to 0.3 V vs RHE), no significant change in the shape of Pd nanocubes is observed [126]. Thus the degradation of Pd nanocubes is suggested to arise from electro-oxidation of hydrogen, but also the effect of mechanical stress from absorption of hydrogen and surface oxidation cannot be excluded. In contrast to Pd nanocubes, Pd nanoparticles deposited on nanocarbon support materials have shown a remarkable electrochemical stability in alkaline conditions [127].

More detailed aspects of the uses of shape-controlled metal nanoparticles in electrochemistry can be read elsewhere [128].

9. Concluding remarks

Different palladium-based catalysts have proven to exhibit superior electrocatalytic activity towards the oxygen reduction reaction compared to commercial Pt/C catalysts. It is clear that interactions between the support material and metal nanoparticles can influence the resulting catalysts' activity by modifying the electronic structure, but also by improving the electroactive surface area. Various additives in the catalyst composition may also affect the ORR kinetics by changing the electronic structure of metal nanoparticles or inhibit the reaction by blocking their surface. Strong adsorption of (bi)sulphate anions reduces the ORR activity in sulphuric acid solution. Based on the several researches, the optimum size of Pd nanoparticles has been found to be around 5 nm. The ORR on Pd is a structure sensitive reaction and Pd(100) facet has been found to possess the highest ORR activity among single crystal facets and subsequently Pd nanoparticles that are cubic in shape have been found to have superior ORR activity. In order to increase the electrocatalytic activity for ORR, PdNPs could be bound to nitrogen-containing groups either using organic ligands or modified support. The main obstacle to use Pd-based catalysts in the fuel cells is their low stability, especially in acidic solution. The main goal for further research on Pd-based ORR catalysts should be further improving their activity and durability in the fuel cell conditions, possibly by designing new composite catalysts and nanostructured electrocatalysts. Further decrease of Pd loading is highly desirable in order to reduce the cost of Pd-containing MEAs.

Acknowledgements

This work was financially supported by institutional research funding (IUT20-16) of the Estonian Ministry of Education and Research. We would like to acknowledge the financial support by the EU through the European Regional Development Fund (TK141 “Advanced materials and high-technology devices for energy recuperation systems”).

References:

[1] M.H. Shao, Q.W. Chang, J.P. Dodelet, R. Chenitz, Recent advances in electrocatalysts for oxygen reduction reaction, Chemical Reviews 116(6) (2016) 3594-3657.
[2] L.M. Vracar, D.B. Sepa, A. Damjanovic, Palladium electrode in oxygen-saturated aqueous-solutions – reduction of oxygen in the activation-controlled region, Journal of the Electrochemical Society 133(9) (1986) 1835-1839.
[3] L.M. Vracar, D.B. Sepa, A. Damjanovic, Palladium electrode in oxygen-saturated aqueous-solutions – potential dependent adsorption of oxygen containing species and their effect on oxygen reduction, Journal of the Electrochemical Society 136(7) (1989) 1973-1977.
[4] M.R. Tarasevich, Investigation of the parallel and consecutive steps in the reactions of oxygen and hydrogen peroxide IX. The mechanism of oxygen electroreduction on the platinum metals, Elektrokhimiya 9 (1973) 599.

[5] I. Srejic, Z. Rakocevic, M. Nenadovic, S. Strbac, Oxygen reduction on polycrystalline palladium in acid and alkaline solutions: topographical and chemical Pd surface changes, Electrochimica Acta 169(0) (2015) 22-31.

[6] S. Kondo, M. Nakamura, N. Maki, N. Hoshi, Active sites for the oxygen reduction reaction on the low and high index planes of palladium, Journal of Physical Chemistry C 113(29) (2009) 12625-12628.

[7] A. Hitotsuyanagi, S. Kondo, M. Nakamura, N. Hoshi, Structural effects on the oxygen reduction reaction on n(111)-(100) series of Pd, Journal of Electroanalytical Chemistry 657(1-2) (2011) 123-127.

[8] A.H. Creus, Y. Gimeno, P. Diaz, L. Vazquez, S. Gonzalez, R.C. Salvarezza, A.J. Arvia, Influence of the nanostructure of palladium mesoparticles on the kinetics of molecular oxygen electroreduction, Journal of Physical Chemistry B 108(30) (2004) 10785-10795.

[9] W. Ju, M. Favaro, C. Durante, L. Perini, S. Agnoli, O. Schneider, U. Stimming, G. Granozzi, Pd Nanoparticles deposited on nitrogen-doped HOPG: new insights into the Pd-catalyzed oxygen reduction reaction, Electrochimica Acta 141 (2014) 89-101.

[10] H. Erikson, M. Liik, A. Sarapuu, J. Kozlova, V. Sammelselg, K. Tammeveski, Oxygen reduction on electrodeposited Pd coatings on glassy carbon, Electrochimica Acta 88 (2013) 513-518.

[11] H. Erikson, M. Liik, A. Sarapuu, M. Marandi, V. Sammelselg, K. Tammeveski, Electrocatalysis of oxygen reduction on electrodeposited Pd coatings on gold, Journal of Electroanalytical Chemistry 691(0) (2013) 35-41.

[12] S. Szunerits, R. Boukherroub, Investigation of the electrocatalytic activity of boron-doped diamond electrodes modified with palladium or gold nanoparticles for oxygen reduction reaction in basic medium, Comptes Rendus Chimie 11(9) (2008) 1004-1009.

[13] M. Asnavandi, B.H.R. Suryanto, C. Zhao, Controlled electrodeposition of nanostructured Pd thin films from protic ionic liquids for electrocatalytic oxygen reduction reactions, RSC Advances 5(90) (2015) 74017-74023.

[14] H. Erikson, A. Kasikov, C. Johans, K. Kontturi, K. Tammeveski, A. Sarapuu, Oxygen reduction on Nafion-coated thin-film palladium electrodes, Journal of Electroanalytical Chemistry 652(1-2) (2011) 1-7.

[15] A. Sarapuu, A. Kasikov, N. Wong, C.A. Lucas, G. Sedghi, R.J. Nichols, K. Tammeveski, Electroreduction of oxygen on gold-supported nanostructured palladium films in acid solutions, Electrochimica Acta 55(22) (2010) 6768-6774.

[16] M. Favaro, S. Agnoli, L. Perini, C. Durante, A. Gennaro, G. Granozzi, Palladium nanoparticles supported on nitrogen-doped HOPG: a surface science and electrochemical study, Physical Chemistry Chemical Physics 15(8) (2013) 2923-2931.

[17] L. Arroyo-Ramirez, D. Rodriguez, W. Otano, C.R. Cabrera, Palladium nanoshell catalysts synthesis on highly ordered pyrolytic graphite for oxygen reduction reaction, ACS Applied Materials & Interfaces 4(4) (2012) 2018-2024.

[18] C.C. Chang, T.C. Wen, H.J. Tien, Kinetics of oxygen reduction at oxide-derived Pd electrodes in alkaline solution, Electrochimica Acta 42(4) (1997) 557-565.

[19] M. Kang, Y. Yang, J.H. Shim, S.C. Lee, Y. Lee, C. Lee, Simple electrodeposition of dendritic Pd without supporting electrolyte and its electrocatalytic activity toward oxygen reduction and H_2O_2 sensing, Electroanalysis 25(12) (2013) 2691-2699.

[20] S.M.S. Kumar, J.S. Herrero, S. Irusta, K. Scott, The effect of pretreatment of Vulcan XC-72R carbon on morphology and electrochemical oxygen reduction kinetics of supported Pd nano-particle in acidic electrolyte, Journal of Electroanalytical Chemistry 647(2) (2010) 211-221.

[21] C. Alegre, A. Stassi, E. Modica, C. Lo Vecchio, A.S. Arico, V. Baglio, Investigation of the activity and stability of Pd-based catalysts towards the oxygen reduction (ORR) and evolution reactions (OER) in iron-air batteries, RSC Advances 5(32) (2015) 25424-25427.
[22] G.F. Alvarez, M. Mamlouk, S.M.S. Kumar, K. Scott, Preparation and characterisation of carbon-supported palladium nanoparticles for oxygen reduction in low temperature PEM fuel cells, Journal of Applied Electrochemistry 41(8) (2011) 925-937.
[23] Y.F. Tang, H.M. Zhang, H.X. Zhong, Y.W. Ma, A facile synthesis of Pd/C cathode electrocatalyst for proton exchange membrane fuel cells, International Journal of Hydrogen Energy 36(1) (2011) 725-731.
[24] Y. Luo, J.M. Mora-Hernández, L.A. Estudillo-Wong, E.M. Arce-Estrada, N. Alonso-Vante, Nanostructured palladium tailored via carbonyl chemical route towards oxygen reduction reaction, Electrochimica Acta 173(0) (2015) 771-778.
[25] R. Rego, C. Oliveira, A. Velazquez, P.-L. Cabot, A new route to prepare carbon paper-supported Pd catalyst for oxygen reduction reaction, Electrochemistry Communications 12(6) (2010) 745-748.
[26] R. Rego, M. Cristina Oliveira, F. Alcaide, G. Alvarez, Development of a carbon paper-supported Pd catalyst for PEMFC application, International Journal of Hydrogen Energy 37(8) (2012) 7192-7199.
[27] S. Salome, R. Rego, A. Querejeta, F. Alcaide, M. Cristina Oliveira, An electrochemical route to prepare Pd nanostructures on a gas diffusion substrate for a PEMFC, Electrochimica Acta 106 (2013) 516-524.
[28] R. Rahul, R.K. Singh, B. Bera, R. Devivaraprasad, M. Neergat, The role of surface oxygenated-species and adsorbed hydrogen in the oxygen reduction reaction (ORR) mechanism and product selectivity on Pd-based catalysts in acid media, Physical Chemistry Chemical Physics 17(23) (2015) 15146-55.
[29] T. Kar, R. Devivaraprasad, B. Bera, R. Ramesh, M. Neergat, Investigation on the reduction of the oxides of Pd and graphite in alkaline medium and the simultaneous evolution of oxygen reduction reaction and peroxide generation features, Electrochimica Acta 191 (2016) 81-89.
[30] J.L. Fernandez, K.P. Imaduwage, C.G. Zoskia, Carbon supported noble metal (Pd and Au) catalysts synthesized by an oxide route with high performance for oxygen reduction in acidic media, Electrochimica Acta 180 (2015) 460-470.
[31] L. Jiang, A. Hsu, D. Chu, R. Chen, Oxygen reduction reaction on carbon supported Pt and Pd in alkaline solutions, Journal of the Electrochemical Society 156(3) (2009) B370-B376.
[32] X.R. Ye, Y.H. Lin, C.M. Wai, Decorating catalytic palladium nanoparticles on carbon nanotubes in supercritical carbon dioxide, Chemical Communications (5) (2003) 642-643.
[33] X.R. Ye, Y.H. Lin, C.M. Wang, M.H. Engelhard, Y. Wang, C.M. Wai, Supercritical fluid synthesis and characterization of catalytic metal nanoparticles on carbon nanotubes, Journal of Materials Chemistry 14(5) (2004) 908-913.
[34] Y.H. Lin, X.L. Cui, X.R. Ye, Electrocatalytic reactivity for oxygen reduction of palladium-modified carbon nanotubes synthesized in supercritical fluid, Electrochemistry Communications 7(3) (2005) 267-274.
[35] C.-L. Lee, Y.-C. Huang, L.-C. Kuo, Y.-W. Lin, Preparation of carbon nanotube-supported palladium nanoparticles by self-regulated reduction of surfactant, Carbon 45(1) (2007) 203-206.
[36] C.-L. Lee, Synthesis and electroactivity of carbon-nanomaterials-supported Pd nanoparticles from self-regulated reduction of sodium n-dodecyl sulfate, Journal of Solid State Electrochemistry 11(9) (2007) 1313-1317.

[37] J. Qu, H. Chen, S. Dong, *In situ* fabrication of noble metal nanoparticles modified multiwalled carbon nanotubes and related electrocatalysis, Electroanalysis 20(22) (2008) 2410-2415.

[38] J.-S. Ye, Y.-C. Bai, W.-D. Zhang, Modification of vertically aligned carbon nanotube arrays with palladium nanoparticles for electrocatalytic reduction of oxygen, Microchimica Acta 165(3-4) (2009) 361-366.

[39] S. Chakraborty, C.R. Raj, Electrocatalytic performance of carbon nanotube-supported palladium particles in the oxidation of formic acid and the reduction of oxygen, Carbon 48(11) (2010) 3242-3249.

[40] J.-S. Zheng, X.-S. Zhang, P. Li, J. Zhu, X.-G. Zhou, W.-K. Yuan, Effect of carbon nanofiber microstructure on oxygen reduction activity of supported palladium electrocatalyst, Electrochemistry Communications 9(5) (2007) 895-900.

[41] T.G. Nikiforova, Y.V. Kabeneva, O.A. Runova, Carbon-supported palladium catalysts for fuel cells, Russian Journal of Applied Chemistry 83(6) (2010) 1001-1009.

[42] K. Jukk, N. Alexeyeva, C. Johans, K. Kontturi, K. Tammeveski, Oxygen reduction on Pd nanoparticle/multi-walled carbon nanotube composites, Journal of Electroanalytical Chemistry 666 (2012) 67-75.

[43] D. Wang, S. Lu, S.P. Jiang, Pd/HPW-PDDA-MWCNTs as effective non-Pt electrocatalysts for oxygen reduction reaction of fuel cells, Chemical Communications 46(12) (2010) 2058-2060.

[44] D. Wang, S. Lu, P.J. Kulesza, C.M. Li, R. De Marco, S.P. Jiang, Enhanced oxygen reduction at Pd catalytic nanoparticles dispersed onto heteropolytungstate-assembled poly(diallyldimethylammonium)-functionalized carbon nanotubes, Physical Chemistry Chemical Physics 13(10) (2011) 4400-4410.

[45] K. Jukk, N. Alexeyeva, A. Sarapuu, P. Ritslaid, J. Kozlova, V. Sammelselg, K. Tammeveski, Electroreduction of oxygen on sputter-deposited Pd nanolayers on multi-walled carbon nanotubes, International Journal of Hydrogen Energy 38(9) (2013) 3614-3620.

[46] K. Jukk, N. Alexeyeva, P. Ritslaid, J. Kozlova, V. Sammelselg, K. Tammeveski, Electrochemical reduction of oxygen on heat-treated Pd nanoparticle/multi-walled carbon nanotube composites in alkaline solution, Electrocatalysis 4(1) (2013) 42-48.

[47] Y.S. Li, T.S. Zhao, Ultra-low catalyst loading cathode electrode for anion-exchange membrane fuel cells, International Journal of Hydrogen Energy 37(20) (2012) 15334-15338.

[48] S. Takenaka, N. Susuki, H. Miyamoto, E. Tanabe, H. Matsunea, M. Kishida, Highly durable Pd metal catalysts for the oxygen reduction reaction in fuel cells; coverage of Pd metal with silica, Chemical Communications 46(47) (2010) 8950-8952.

[49] S. Takenaka, N. Susuki, H. Miyamoto, E. Tanabe, H. Matsune, M. Kishida, Highly durable carbon nanotube-supported Pd catalysts covered with silica layers for the oxygen reduction reaction, Journal of Catalysis 279(2) (2011) 381-388.

[50] M.S. Ahmed, H. Jeong, J.-M. You, S. Jeon, Electrocatalytic reduction of dioxygen at a modified glassy carbon electrode based on Nafion®-dispersed single-walled carbon nanotubes and cobalt-porphyrin with palladium nanoparticles in acidic media, Electrochimica Acta 56(13) (2011) 4924-4929.

[51] E.P. Randviir, D.A.C. Brownson, C.E. Banks, A decade of graphene research: production, applications and outlook, Materials Today 17(9) (2014) 426-432.

[52] M.H. Seo, S.M. Choi, H.J. Kim, W.B. Kim, The graphene-supported Pd and Pt catalysts for highly active oxygen reduction reaction in an alkaline condition, Electrochemistry Communications 13(2) (2011) 182-185.

[53] M.H. Seo, S.M. Choi, D.U. Lee, W.B. Kim, Z. Chen, Correlation between theoretical descriptor and catalytic oxygen reduction activity of graphene supported palladium and palladium alloy electrocatalysts, Journal of Power Sources 300 (2015) 1-9.

[54] C.-T. Hsieh, Y.-Y. Liu, A.K. Roy, Pulse electrocleposited Pd nanoclusters on graphene-based electrodes for proton exchange membrane fuel cells, Electrochimica Acta 64 (2012) 205-210.

[55] C.-T. Hsieh, J.-L. Gu, Y.-C. Chen, D.-Y. Tzou, Pulse microwave synthesis of palladium catalysts on graphene electrodes for proton exchange membrane fuel cells, Electrochimica Acta 98 (2013) 39-47.

[56] K. Kakaei, H. Gharibi, Palladium nanoparticle catalysts synthesis on graphene in sodium dodecyl sulfate for oxygen reduction reaction, Energy 65 (2014) 166-171.

[57] D. Kim, M.S. Ahmed, S. Jeon, Different length linkages of graphene modified with metal nanoparticles for oxygen reduction in acidic media, Journal of Materials Chemistry 22(32) (2012) 16353-16360.

[58] J.E. Choe, M.S. Ahmed, S. Jeon, 3,4-Ethylenedioxythiophene functionalized graphene with palladium nanoparticles for enhanced electrocatalytic oxygen reduction reaction, Journal of Power Sources 281 (2015) 211-218.

[59] S. Yun, S. Lee, C. Shin, S. Park, S.J. Kwon, H.S. Park, One-Pot Self-assembled, reduced graphene oxide/palladium nanoparticle hybrid aerogels for electrocatalytic applications, Electrochimica Acta 180 (2015) 902-908.

[60] Y.X. Huang, J.F. Xie, X. Zhang, L. Xiong, H.Q. Yu, Reduced graphene oxide supported palladium nanoparticles via photoassisted citrate reduction for enhanced electrocatalytic activities, ACS Applied Materials & Interfaces 6(18) (2014) 15795-15801.

[61] C.P. Deming, R. Mercado, V. Gadiraju, S.W. Sweeney, M. Khan, S. Chen, Graphene quantum dots-supported palladium nanoparticles for efficient electrocatalytic reduction of oxygen in alkaline media, ACS Sustainable Chemistry & Engineering 3(12) (2015) 3315-3323.

[62] Z.-T. Liu, K.-L. Huang, Y.-S. Wu, Y.-P. Lyu, C.-L. Lee, A comparison of physically and chemically defective graphene nanosheets as catalyst supports for cubic Pd nanoparticles in an alkaline oxygen reduction reaction, Electrochimica Acta 186 (2015) 552-561.

[63] R. Carrera-Cerritos, V. Baglio, A.S. Arico, J. Ledesma-Garcia, M.F. Sgroi, D. Pullini, A.J. Pruna, D.B. Mataix, R. Fuentes-Ramirez, L.G. Arriaga, Improved Pd electro-catalysis for oxygen reduction reaction in direct methanol fuel cell by reduced graphene oxide, Applied Catalysis B-Environmental 144 (2014) 554-560.

[64] R. Bashyam, P. Zelenay, A class of non-precious metal composite catalysts for fuel cells, Nature 443(7107) (2006) 63-66.

[65] L. Perini, C. Durante, M. Favaro, V. Perazzolo, S. Agnoli, O. Schneider, G. Granozzi, A. Gennaro, Metal-support interaction in platinum and palladium nanoparticles loaded on nitrogen-doped mesoporous carbon for oxygen reduction reaction, ACS Applied Materials & Interfaces 7(2) (2015) 1170-1179.

[66] K. Jukk, N. Kongi, L. Matisen, T. Kallio, K. Kontturi, K. Tammeveski, Electroreduction of oxygen on palladium nanoparticles supported on nitrogen-doped graphene nanosheets, Electrochimica Acta 137 (2014) 206-212.

[67] B.P. Vinayan, K. Sethupathi, S. Ramaprabhu, Facile synthesis of triangular shaped palladium nanoparticles decorated nitrogen doped graphene and their catalytic study for renewable energy applications, International Journal of Hydrogen Energy 38(5) (2013) 2240-2250.

[68] D. Ye, R. Zhang, Y. Fu, J. Bu, Y. Wang, B. Liu, J. Kong, Co-calcination-derived Pd budded in N-doped ordered mesoporous graphitic carbon nanospheres for advanced methanol-tolerant oxygen reduction, Electrochimica Acta 160(0) (2015) 306-312.

[69] K. Song, Z. Zou, D. Wang, B. Tan, J. Wang, J. Chen, T. Li, Microporous organic polymers derived microporous carbon supported Pd catalysts for oxygen reduction reaction:

impact of framework and heteroatom, Journal of Physical Chemistry C 120(4) (2016) 2187-2197.

[70] L. Song, T. Wang, H. Xue, X. Fan, J. He, *In-situ* preparation of Pd incorporated ordered mesoporous carbon as efficient electrocatalyst for oxygen reduction reaction, Electrochimica Acta 191 (2016) 355-363.

[71] S.K. Konda, M. Amiri, A.C. Chen, Photoassisted deposition of palladium nanoparticles on carbon nitride for efficient oxygen reduction, Journal of Physical Chemistry C 120(27) (2016) 14467-14473.

[72] T. Bhowmik, M.K. Kundu, S. Barman, Highly active and durable Pd nanoparticles-porous graphitic carbon nitride composite for electrocatalytic oxygen reduction reaction, International Journal of Hydrogen Energy 41(33) (2016) 14768-14777.

[73] X. Li, C. Lin, C. Batchelor-McAuley, E. Laborda, L. Shao, R.G. Compton, New insights into fundamental electron transfer from single nanoparticle voltammetry, The Journal of Physical Chemistry Letters 7(8) (2016) 1554-1558.

[74] K.C. Poon, D.C.L. Tan, T.D.T. Vo, B. Khezri, H. Su, R.D. Webster, H. Sato, Newly developed stepwise electroless deposition enables a remarkably facile synthesis of highly active and stable amorphous Pd nanoparticle electrocatalysts for oxygen reduction reaction, Journal of the American Chemical Society 136(14) (2014) 5217-5220.

[75] T.-Y. Jeon, S.J. Yoo, H.-Y. Park, S.-K. Kim, S. Lim, D. Peck, D.-H. Jung, Y.-E. Sung, Electrocatalytic effects of carbon dissolution in Pd nanoparticles, Langmuir 28(7) (2012) 3664-3670.

[76] C. Jeyabharathi, P. Venkateshkumar, J. Mathiyarasu, K.L.N. Phani, Carbon-supported palladium-polypyrrole nanocomposite for oxygen reduction and its tolerance to methanol, Journal of the Electrochemical Society 157(11) (2010) B1740-B1745.

[77] M. Goral-Kurbiel, A. Drelinkiewicz, R. Kosydar, B. Dembinska, P.J. Kulesza, J. Gurgul, Palladium content effect on the electrocatalytic activity of palladium-polypyrrole nanocomposite for cathodic reduction of oxygen, Electrocatalysis 5(1) (2014) 23-40.

[78] G. Fu, X. Jiang, L. Tao, Y. Chen, J. Lin, Y. Zhou, Y. Tang, T. Lu, Polyallylamine functionalized palladium icosahedra: one-pot water-based synthesis and their superior electrocatalytic activity and ethanol tolerant ability in alkaline media, Langmuir 29(13) (2013) 4413-4420.

[79] Y. Shi, S. Yin, Y. Ma, D. Lu, Y. Chen, Y. Tang, T. Lu, Oleylamine-functionalized palladium nanoparticles with enhanced electrocatalytic activity for the oxygen reduction reaction, Journal of Power Sources 246 (2014) 356-360.

[80] Y.H. Xue, L. Zhang, W.J. Zhou, S.H. Chan, Pd nanoparticles supported on PDDA-functionalized carbon black with enhanced ORR activity in alkaline medium, International Journal of Hydrogen Energy 39(16) (2014) 8449-8456.

[81] M. Goral-Kurbiel, A. Drelinkiewicz, R. Kosydar, J. Gurgul, B. Dembinska, P.J. Kulesza, The effect of Nafion ionomer on electroactivity of palladium-polypyrrole catalysts for oxygen reduction reaction, Journal of Solid State Electrochemistry 18(3) (2014) 639-653.

[82] S. Zhao, H. Zhang, S.D. House, R. Jin, J.C. Yang, R. Jin, Ultrasmall palladium nanoclusters as effective catalyst for oxygen reduction reaction, ChemElectroChem 3(8) (2016) 1225-1229.

[83] N. Naresh, F.G.S. Wasim, B.P. Ladewig, M. Neergat, Removal of surfactant and capping agent from Pd nanocubes (Pd-NCs) using tert-butylamine: its effect on electrochemical characteristics, Journal of Materials Chemistry A 1(30) (2013) 8553-8559.

[84] N. Nalajala, W.F.G. Saleha, B.P. Ladewig, M. Neergat, Sodium borohydride treatment: a simple and effective process for the removal of stabilizer and capping agents from shape-controlled palladium nanoparticles, Chemical Communications 50(66) (2014) 9365-9368.

[85] Z. Mojovic, T. Mudrinic, P. Bankovic, N. Jovic-Jovicic, A. Ivanovic-Sasic, A. Milutinovic-Nikolic, D. Jovanovic, Oxygen reduction reaction on palladium-modified zeolite 13X, Journal of Solid State Electrochemistry 19(7) (2015) 1993-2000.
[86] C. Lo Vecchio, C. Alegre, D. Sebastian, A. Stassi, A.S. Arico, V. Baglio, Investigation of supported Pd-based electrocatalysts for the oxygen reduction reaction: performance, durability and methanol tolerance, Materials 8(12) (2015) 7997-8008.
[87] S.J. Bae, K.S. Nahm, P. Kim, Electroreduction of oxygen on Pd catalysts supported on Ti-modified carbon, Current Applied Physics 12(6) (2012) 1476-1480.
[88] S. Maheswari, P. Sridhar, S. Pitchumani, Pd-TiO_2/C as a methanol tolerant catalyst for oxygen reduction reaction in alkaline medium, Electrochemistry Communications 26 (2013) 97-100.
[89] W. Sun, A. Hsu, R. Chen, Palladium-coated manganese dioxide catalysts for oxygen reduction reaction in alkaline media, Journal of Power Sources 196(10) (2011) 4491-4498.
[90] H.-Q. Dong, Y.-Y. Chen, M. Han, S.-L. Li, J. Zhang, J.-S. Li, Y.-Q. Lan, Z.-H. Dai, J.-C. Bao, Synergistic effect of mesoporous Mn_2O_3-supported Pd nanoparticle catalysts for electrocatalytic oxygen reduction reaction with enhanced performance in alkaline medium, Journal of Materials Chemistry A 2(5) (2014) 1272-1276.
[91] Q. Wu, Z. Rao, L. Yuan, L. Jiang, G. Sun, J. Ruan, Z. Zhou, S. Sang, Carbon supported PdO with improved activity and stability for oxygen reduction reaction in alkaline solution, Electrochimica Acta 150 (2014) 157-166.
[92] C.H. Choi, S.H. Park, S.I. Woo, Oxygen reduction activity of Pd-Mn_3O_4 nanoparticles and performance enhancement by voltammetrically accelerated degradation, Physical Chemistry Chemical Physics 14(19) (2012) 6842-6848.
[93] C.S. Sharma, R. Awasthi, R.N. Singh, A.S.K. Sinha, Graphene-cobaltite-Pd hybrid materials for use as efficient bifunctional electrocatalysts in alkaline direct methanol fuel cells, Physical Chemistry Chemical Physics 15(46) (2013) 20333-20344.
[94] I.-T. Kim, M. Choi, H.-K. Lee, J. Shim, Characterization of methanol-tolerant Pd-WO_3 and Pd-SnO_2 electrocatalysts for the oxygen reduction reaction in direct methanol fuel cells, Journal of Industrial and Engineering Chemistry 19(3) (2013) 813-818.
[95] Z. Zhang, X. Wang, Z. Cui, C. Liu, T. Lu, W. Xing, Pd nanoparticles supported on WO_3/C hybrid material as catalyst for oxygen reduction reaction, Journal of Power Sources 185(2) (2008) 941-945.
[96] S.-a. Jin, K. Kwon, C. Pak, H. Chang, The oxygen reduction electrocatalytic activity of intermetallic compound of palladium-tin supported on tin oxide-carbon composite, Catalysis Today 164(1) (2011) 176-180.
[97] Z. Yan, M. Zhang, J. Xie, J. Zhu, P.K. Shen, A bimetallic carbide Fe_2MoC promoted Pd electrocatalyst with performance superior to Pt/C towards the oxygen reduction reaction in acidic media, Applied Catalysis B-Environmental 165 (2015) 636-641.
[98] Z. Li, S. Ji, B.G. Pollet, P.K. Shen, A Co_3W_3C promoted Pd catalyst exhibiting competitive performance over Pt/C catalysts towards the oxygen reduction reaction, Chemical Communications 50(5) (2014) 566-568.
[99] J. Ma, A. Habrioux, N. Alonso-Vante, The effect of substrates at cathodes in low-temperature fuel cells, ChemElectroChem 1(1) (2014) 37-46.
[100] X. Xie, Y. Nie, S. Chen, W. Ding, X. Qi, L. Li, Z. Wei, A catalyst superior to carbon-supported-platinum for promotion of the oxygen reduction reaction: reduced-polyoxometalate supported palladium, Journal of Materials Chemistry A 3(26) (2015) 13962-13969.
[101] L. Jiang, A. Hsu, D. Chu, R. Chen, Size-dependent activity of palladium nanoparticles for oxygen electroreduction in alkaline solutions, Journal of the Electrochemical Society 156(5) (2009) B643-B649.

[102] A. Anastasopoulos, J.C. Davies, L. Hannah, B.E. Hayden, C.E. Lee, C. Milhano, C. Mormiche, L. Offin, The particle size dependence of the oxygen reduction reaction for carbon-supported platinum and palladium, ChemSusChem 6(10) (2013) 1973-1982.

[103] W.J. Zhou, M. Li, O.L. Ding, S.H. Chan, L. Zhang, Y.H. Xue, Pd particle size effects on oxygen electrochemical reduction, International Journal of Hydrogen Energy 39(12) (2014) 6433-6442.

[104] W. Ju, T. Bruelle, M. Favaro, L. Perini, C. Durante, O. Schneider, U. Stimming, Palladium nanoparticles supported on highly oriented pyrolytic graphite: preparation, reactivity and stability, ChemElectroChem 2(4) (2015) 547-558.

[105] E. Antolini, Structural parameters of supported fuel cell catalysts: the effect of particle size, inter-particle distance and metal loading on catalytic activity and fuel cell performance, Applied Catalysis B-Environmental 181 (2016) 298-313.

[106] A.R. Tao, S. Habas, P. Yang, Shape control of colloidal metal nanocrystals, Small 4(3) (2008) 310-325.

[107] M. Shao, T. Yu, J.H. Odell, M. Jin, Y. Xia, Structural dependence of oxygen reduction reaction on palladium nanocrystals, Chemical Communications 47(23) (2011) 6566-6568.

[108] M.H. Shao, J. Odell, M. Humbert, T.Y. Yu, Y.N. Xia, Electrocatalysis on shape-controlled palladium nanocrystals: oxygen reduction reaction and formic acid oxidation, Journal of Physical Chemistry C 117(8) (2013) 4172-4180.

[109] H. Erikson, A. Sarapuu, K. Tammeveski, J. Solla-Gullon, J.M. Feliu, Enhanced electrocatalytic activity of cubic Pd nanoparticles towards the oxygen reduction reaction in acid media, Electrochemistry Communications 13(7) (2011) 734-737.

[110] H. Erikson, A. Sarapuu, N. Alexeyeva, K. Tammeveski, J. Solla-Gullon, J.M. Feliu, Electrochemical reduction of oxygen on palladium nanocubes in acid and alkaline solutions, Electrochimica Acta 59 (2012) 329-335.

[111] H. Erikson, M. Lüsi, A. Sarapuu, K. Tammeveski, J. Solla-Gullon, J.M. Feliu, Oxygen electroreduction on carbon-supported Pd nanocubes in acid solutions, Electrochimica Acta 188 (2016) 301-308.

[112] M. Lüsi, H. Erikson, A. Sarapuu, K. Tammeveski, J. Solla-Gullon, J.M. Feliu, Oxygen reduction reaction on carbon-supported palladium nanocubes in alkaline media, Electrochemistry Communications 64 (2016) 9-13.

[113] C.L. Lee, H.P. Chiou, C.R. Liu, Palladium nanocubes enclosed by (100) planes as electrocatalyst for alkaline oxygen electroreduction, International Journal of Hydrogen Energy 37(5) (2012) 3993-3997.

[114] C.-L. Lee, H.-P. Chiou, Methanol-tolerant Pd nanocubes for catalyzing oxygen reduction reaction in H_2SO_4 electrolyte, Applied Catalysis B-Environmental 117 (2012) 204-211.

[115] N. Arjona, M. Guerra-Balcazar, L. Ortiz-Frade, G. Osorio-Monreal, L. Alvarez-Contreras, J. Ledesma-Garcia, L.G. Arriaga, Electrocatalytic activity of well-defined and homogeneous cubic-shaped Pd nanoparticles, Journal of Materials Chemistry A 1(48) (2013) 15524-15529.

[116] K.-L. Huang, Z.-T. Liu, C.-L. Lee, Truncated palladium nanocubes: synthesis and the effect of OH^- concentration on their catalysis of the alkaline oxygen reduction reaction, Electrochimica Acta 157 (2015) 78-87.

[117] M. Arenz, T.J. Schmidt, K. Wandelt, P.N. Ross, N.M. Markovic, The oxygen reduction reaction on thin palladium films supported on a Pt(111) electrode, Journal of Physical Chemistry B 107(36) (2003) 9813-9819.

[118] S. Choi, H. Jeong, K.H. Choi, J.Y. Song, J. Kim, Electrodeposition of triangular Pd rod nanostructures and their electrocatalytic and SERS activities, ACS Applied Materials & Interfaces 6(4) (2014) 3002-3007.

[119] D. Faggion, R. Haddad, F. Giroud, M. Holzinger, C.E.M. de Campos, J.J.S. Acuna, J.B. Domingos, S. Cosnier, Cubic PdNP-based air-breathing cathodes integrated in glucose hybrid biofuel cells, Nanoscale 8(19) (2016) 10433-10440.

[120] L. Xiao, L. Zhuang, Y. Liu, J. Lu, H.D. Abruna, Activating Pd by morphology tailoring for oxygen reduction, Journal of the American Chemical Society 131(2) (2009) 602-608.

[121] Y. Cai, C. Ma, Y.M. Zhu, J.X. Wang, R.R. Adzic, Low-coordination sites in oxygen-reduction electrocatalysis: their roles and methods for removal, Langmuir 27(13) (2011) 8540-8547.

[122] K.K. Maniam, R. Chetty, Electrodeposited palladium nanoflowers for electrocatalytic applications, Fuel Cells 13(6) (2013) 1196-1204.

[123] S.R. Brankovic, J.X. Wang, R.R. Adzic, Metal monolayer deposition by replacement of metal adlayers on electrode surfaces, Surface Science 474(1-3) (2001) L173-L179.

[124] Y.-B. Cho, J.E. Kim, J.H. Shim, C. Lee, Y. Lee, Synthesis and electrocatalytic activity of highly porous hollow palladium nanoshells for oxygen reduction in alkaline solution, Physical Chemistry Chemical Physics 15(27) (2013) 11461-11467.

[125] S.M. Alia, K. Duong, T. Liu, K. Jensen, Y. Yan, Palladium and gold nanotubes as oxygen reduction reaction and alcohol oxidation reaction catalysts in base, ChemSusChem 7(6) (2014) 1739-1744.

[126] A. Zadick, L. Dubau, A. Zalineeva, C. Coutanceau, M. Chatenet, When cubic nanoparticles get spherical: an identical location transmission electron microscopy case study with Pd in alkaline media, Electrochemistry Communications 48 (2014) 1-4.

[127] C.A. Martins, P.S. Fernández, F. de Lima, H.E. Troiani, M.E. Martins, A. Arenillas, G. Maia, G.A. Camara, Remarkable electrochemical stability of one-step synthesized Pd nanoparticles supported on graphene and multi-walled carbon nanotubes, Nano Energy 9 (2014) 142-151.

[128] F.J. Vidal-Iglesias, J. Solla-Gullón, J.M. Feliu, Recent advances in the use of shape-controlled metal nanoparticles in electrocatalysis, in: I.K. Ozoemena, S. Chen (Eds.), Nanomaterials for fuel cell catalysis, Springer International Publishing, Cham, 2016, pp. 31-92.

Figure captions

Figure 1. Voltammograms of the oxygen reduction reaction using a rotating disk electrode in 0.1 M $HClO_4$ saturated with O_2. Rotation rate: 2000 rpm. Scanning rate: 0.010 V s^{-1}. The low index planes of Pd. The result of Pt(110) is also shown for comparison. The inset shows the hard sphere models of the low index planes. Reprinted with permission from [6]. Copyright 2009 American Chemical Society.

Figure 2. RDE voltammetry curves for O_2 reduction on Pd thin-films evaporated onto Au (a, b) and glassy carbon (c) and bulk Pd electrodes in (a) O_2-saturated 0.1 M $HClO_4$, (b) 0.05 M H_2SO_4 and (c) in 0.1 M KOH. Electrode rotation rate: 1900 rpm; scan rate 10 mV s^{-1}. Reprinted with permission from [14, 15]. Copyright 2009 Elsevier.

Figure 3. Linear sweep voltammograms of O_2 reduction on Pd/C catalysts prepared using various reducing agents: ethylene glycol (Pd/C-EG), formaldehyde (Pd/C-CH_2O) and $NaBH_4$ (Pd/C-$NaBH_4$) and Pd/C(Etek), Pt/C(Etek). in O_2 saturated 0.5 M H_2SO_4 solution. Scan rate 1 mV s^{-1}, metal loading 86 µg cm^{-2}. LSVs are compared with those of the commercial Pd/C and Pt/C from Etek. Reprinted with permission from [22]. Copyright 2009 Springer.

Figure 4. Comparison of the polarisation curves of ORR on graphene nanosheets supported Pd and Pt catalysts in O_2-saturated 0.1 M NaOH solution. Sweep rate: 10 mV s^{-1}; rotating speed: 1600 rpm. Reprinted with permission from [52]. Copyright 2009 Elsevier.

Figure 5. TEM images of PdNPs on N-doped ordered mesoporous graphitic carbon nanospheres (Pd/N-MCN). (a) Inset, HRTEM image of Pd/N-MCN. (b) LSVs of mesoporous graphitic carbon nanospheres (MCN), N-doped MCN (N-MCN), PdNPs on MCN (Pd/MCN), Pd/N-MCN and Pt/C in O_2-saturated 0.1 M KOH with a sweep rate of 5 mV/s at a rotation rate of 1600 rpm. Reprinted with permission from [68]. Copyright 2009 Elsevier.

Figure 6. Mass (a) and active surface area (b) normalised Tafel plots of the kinetically controlled ORR currents on the Pd/C catalysts. Particle size: Pd/C-AR – 3.1 nm; Pd/C-300 – 4.7 nm; Pd/C-400 – 4.7 nm; Pd/C-500 – 8.6 nm; Pd/C-600 – 16.7 nm. Reprinted with permission from [101]. Copyright 2009 The Electrochemical Society.

Figure 7. (a) TEM images of cubic PdNPs. A comparison of RDE voltammetry curves on PdNP modified GC electrodes and bulk Pd in O_2-saturated (b) 0.05 M H_2SO_4 and (c) 0.1 M KOH. Electrode rotation speed: 1900 rpm, scan rate: 10 mV s^{-1}. Reprinted with permission from [110]. Copyright 2009

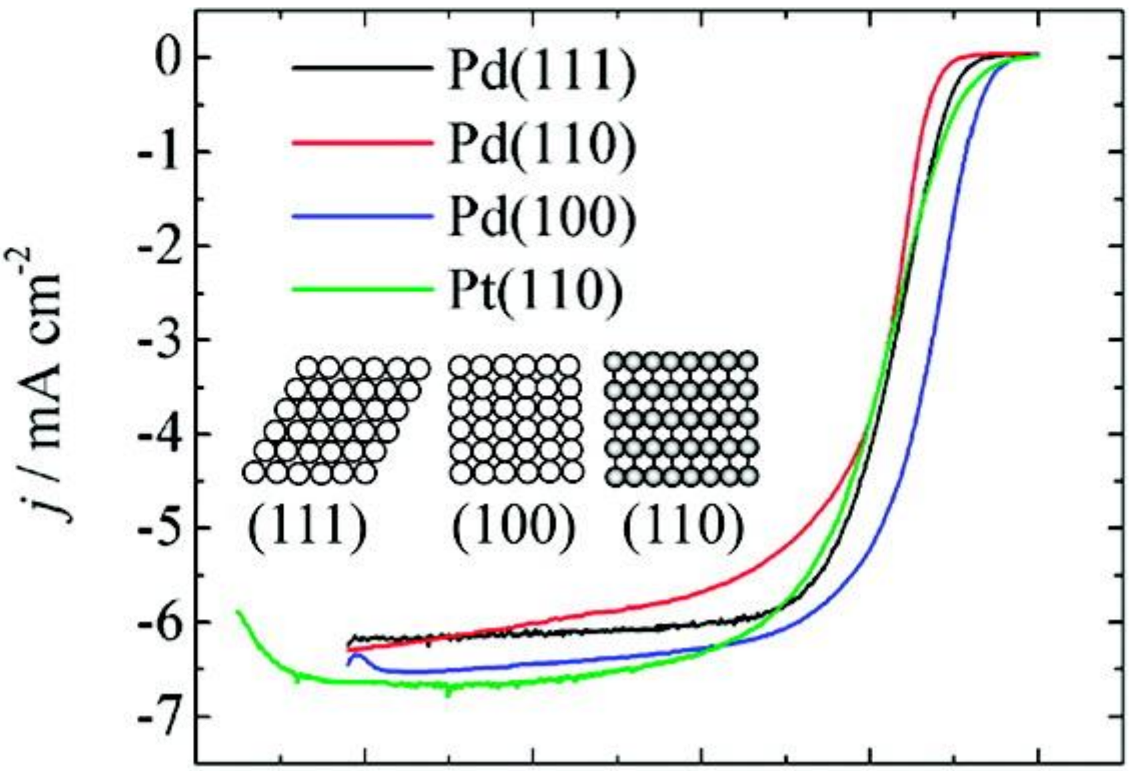

Figure 1

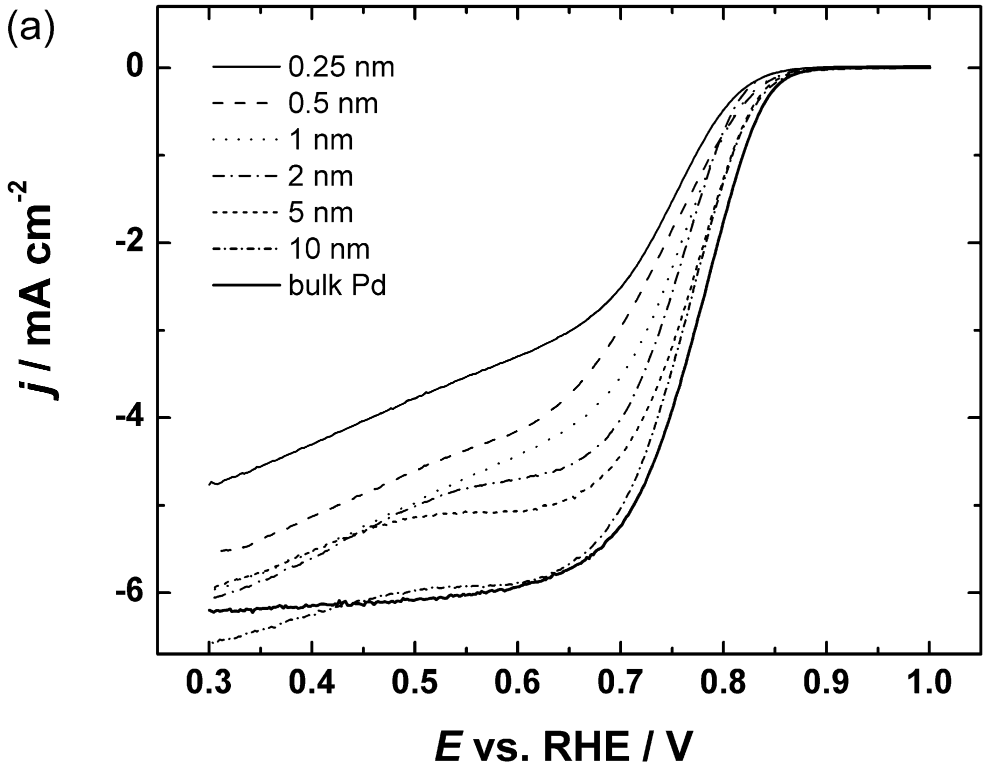
(a)
0.25 nm
0.5 nm
1 nm
2 nm
5 nm
10 nm
bulk Pd
0
-2
-4
-6
j / mA cm^{-2}
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
E vs. RHE / V

Figure 2a

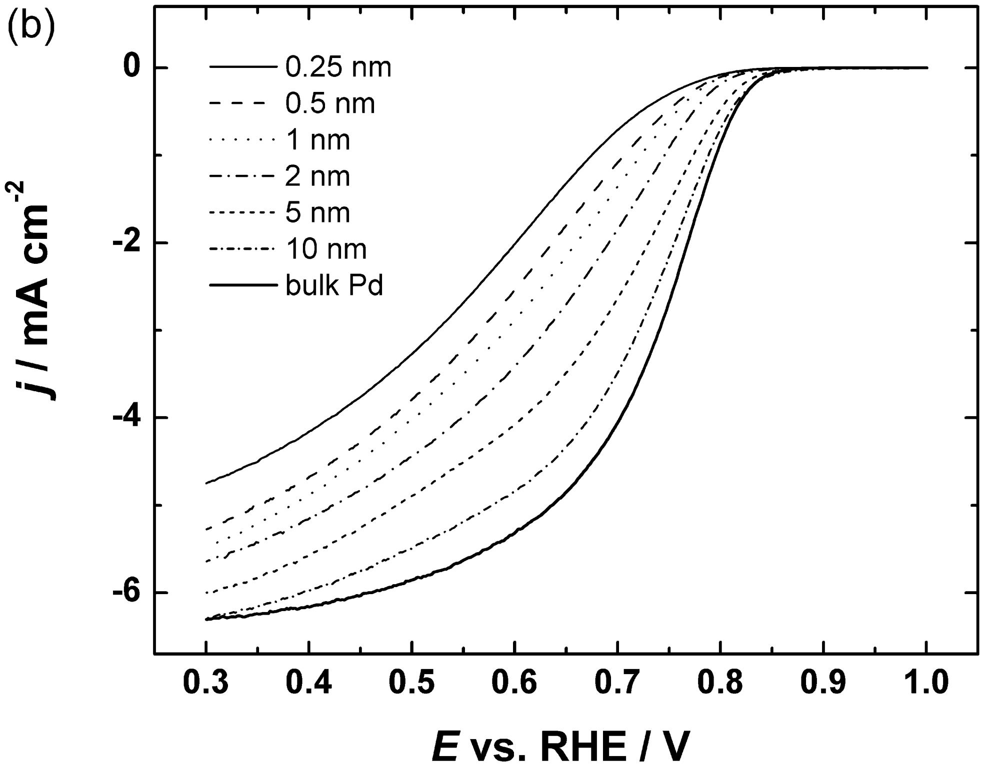
(b)
0.25 nm
0.5 nm
1 nm
2 nm
5 nm
10 nm
bulk Pd
0
-2
-4
-6
j / mA cm^{-2}
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
E vs. RHE / V

Figure 2b

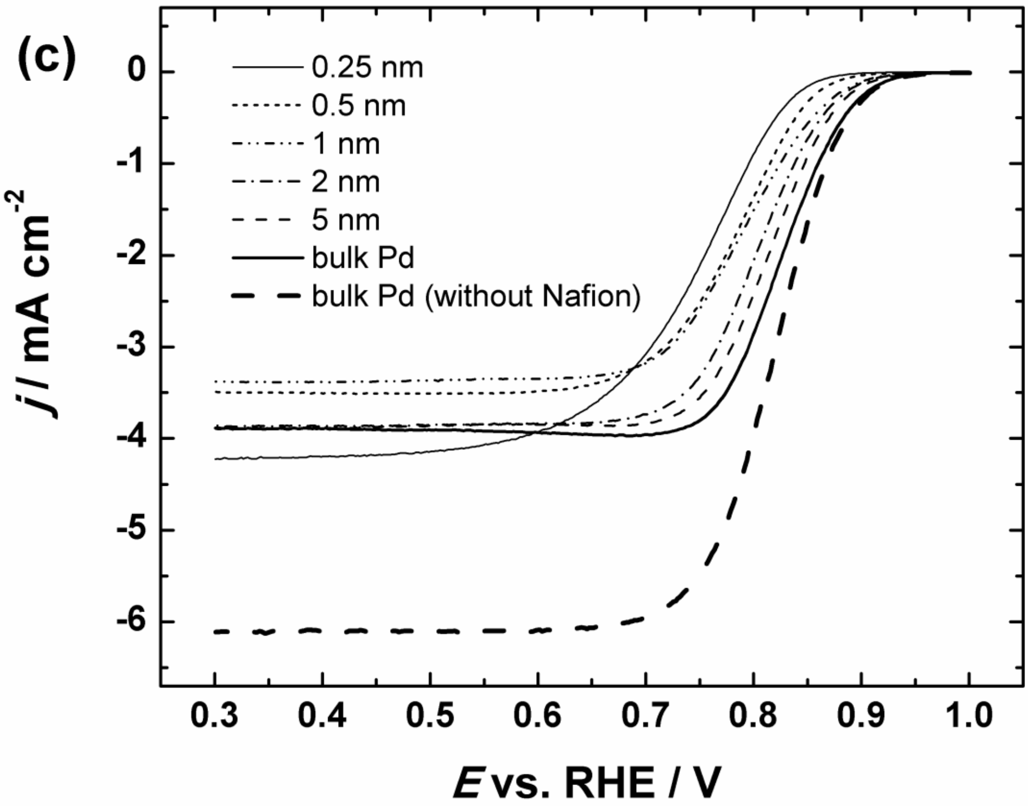
(c)
0.25 nm
0.5 nm
1 nm
2 nm
5 nm
bulk Pd
bulk Pd (without Nafion)
j / mA cm^{-2}
0
-1
-2
-3
-4
-5
-6
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
E vs. RHE / V

Figure 2c

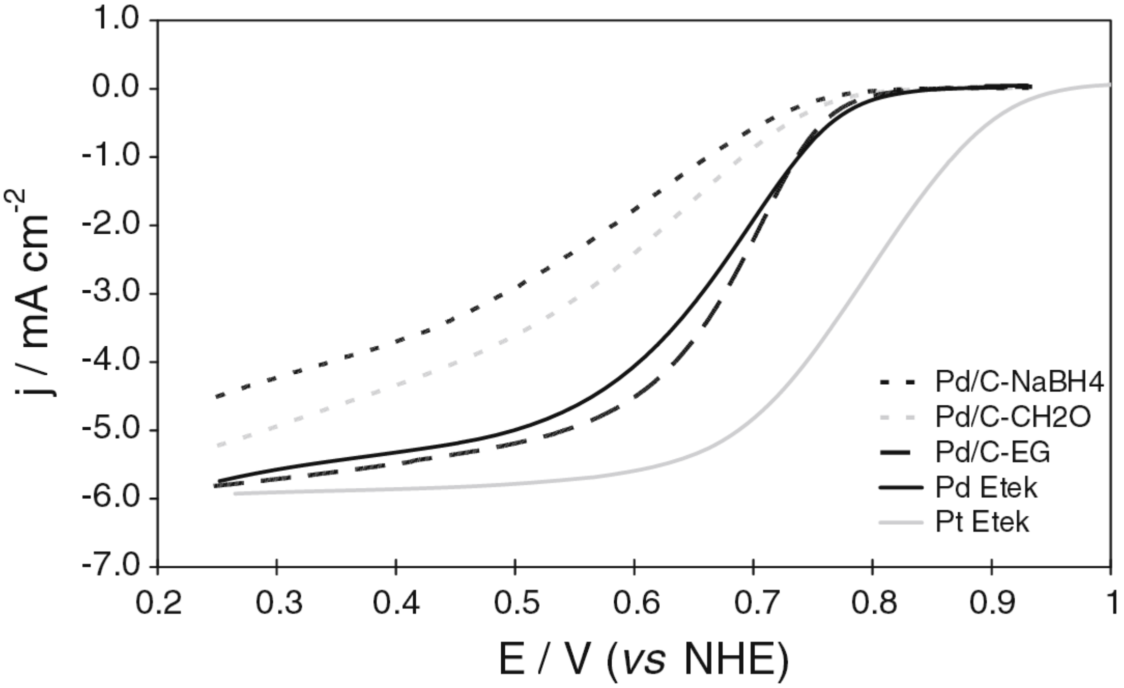
1.0
0.0
-1.0
-2.0
-3.0
-4.0
-5.0
-6.0
-7.0
j / mA cm-2
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
E / V (vs NHE)
Pd/C-NaBH4
Pd/C-CH2O
Pd/C-EG
Pd Etek
Pt Etek

Figure 3

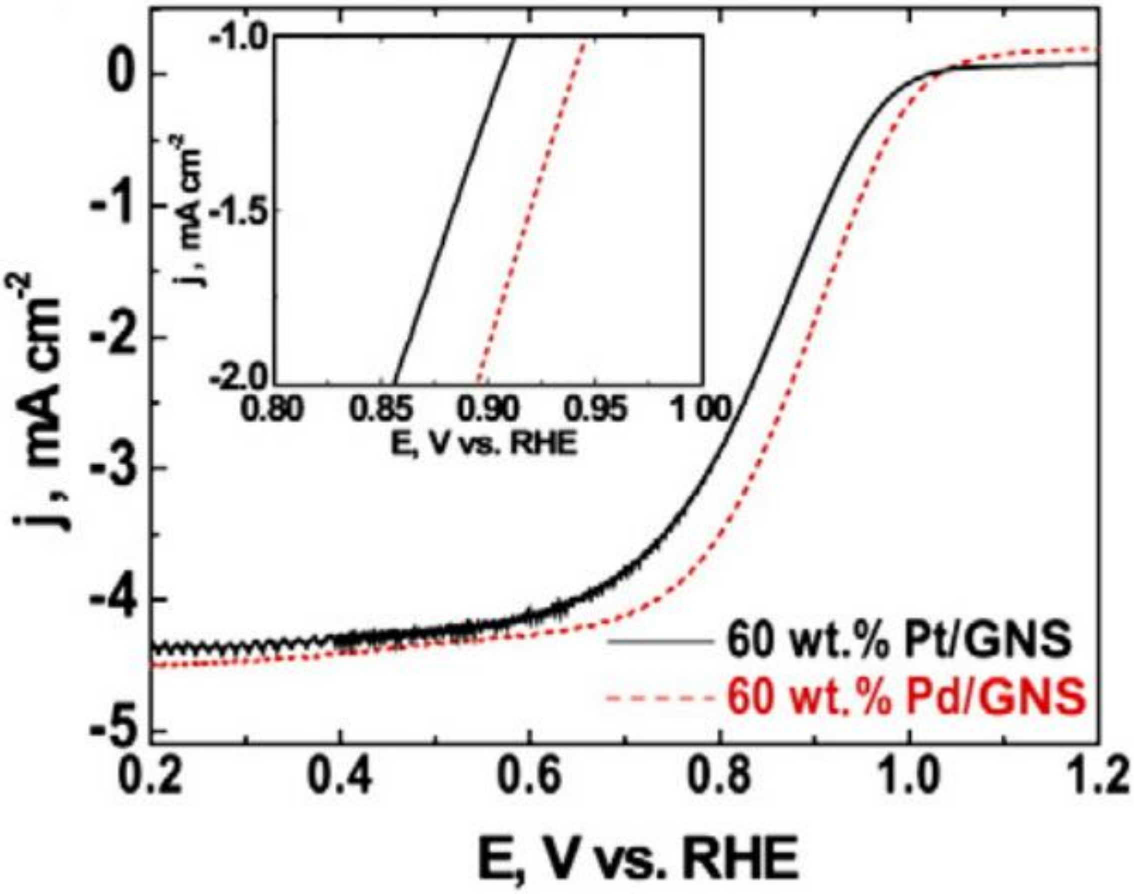
j , mA cm^{-2}
0
-1
-2
-3
-4
-5
0.2
0.4
0.6
0.8
1.0
1.2
E, V vs. RHE
60 wt.% Pt/GNS
60 wt.% Pd/GNS
j , mA cm^{-2}
-1.0
-1.5
-2.0
0.80
0.85
0.90
0.95
1.00
E, V vs. RHE

Figure 4

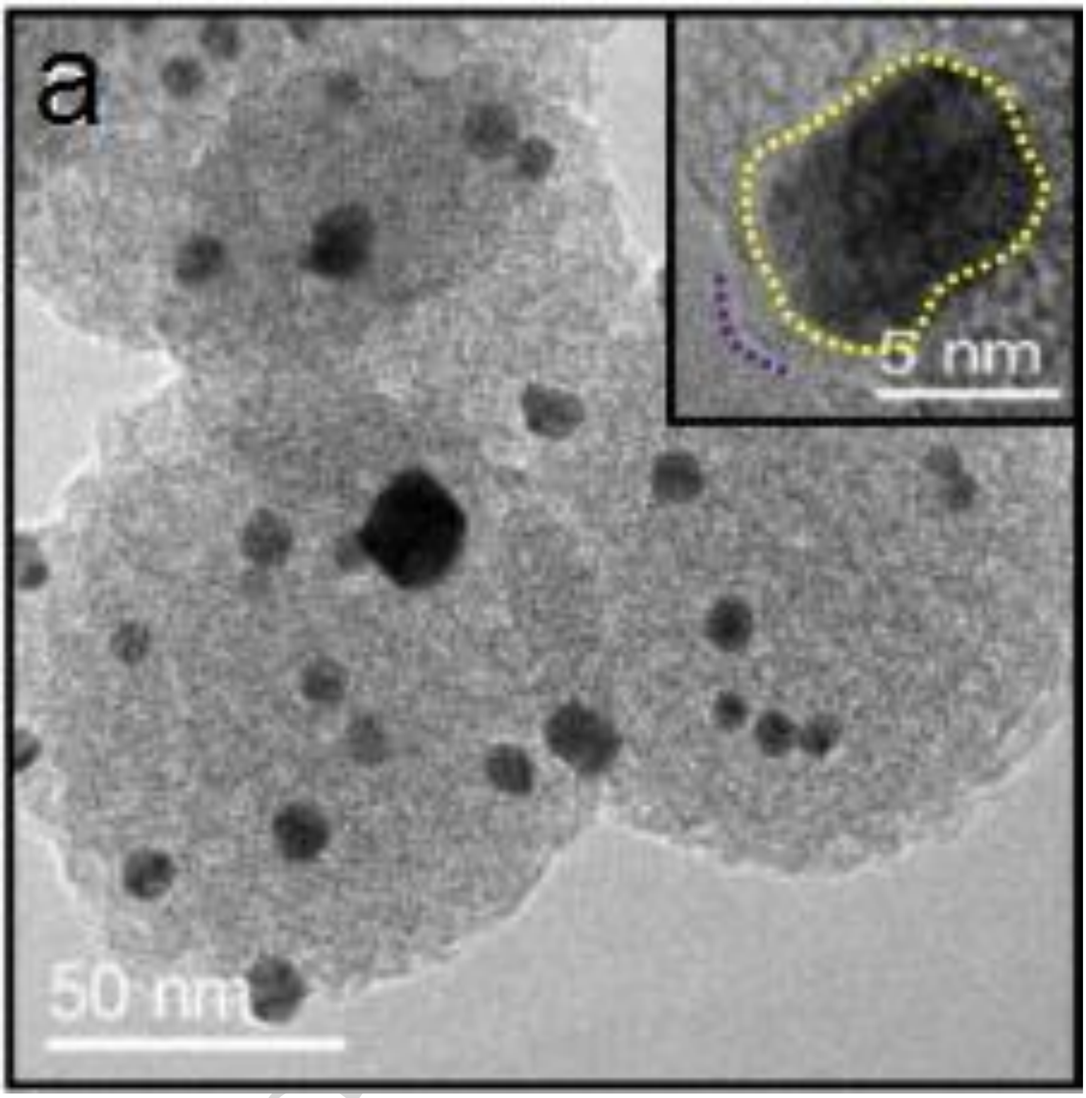

Figure 5a

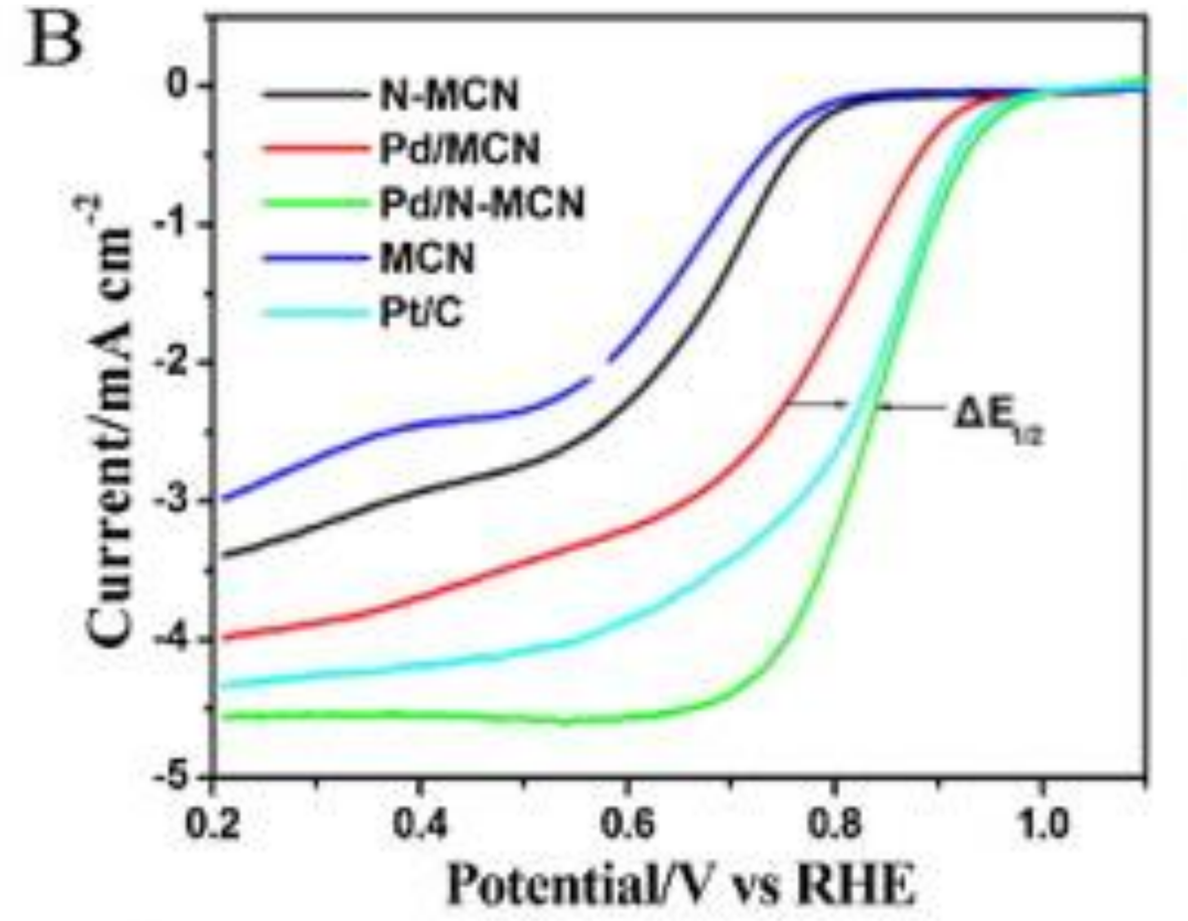
B
N-MCN
Pd/MCN
Pd/N-MCN
MCN
Pt/C
$\Delta E_{1/2}$
Current/mA cm^{-2}
0
-1
-2
-3
-4
-5
0.2
0.4
0.6
0.8
1.0
Potential/V vs RHE

Figure 5b

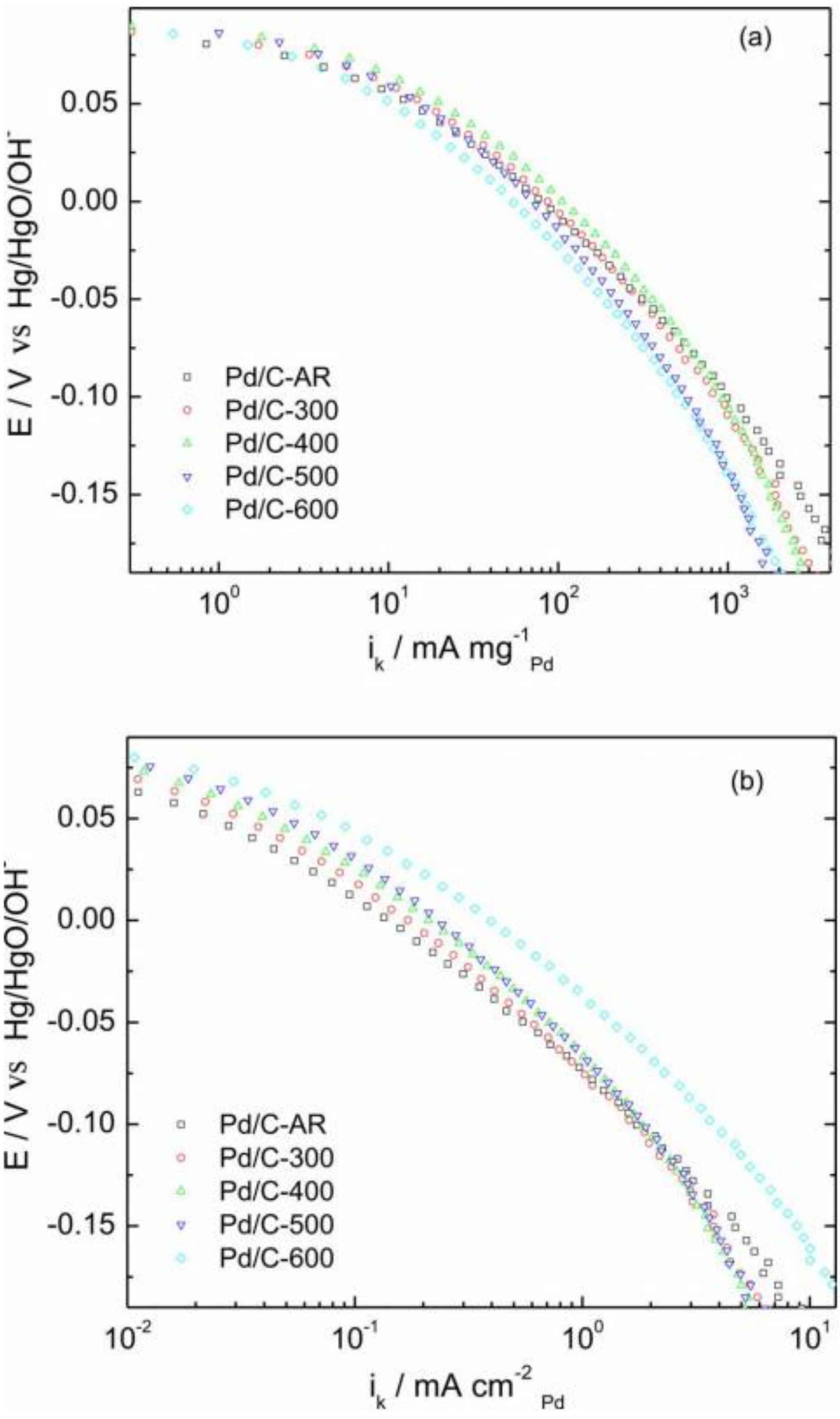
(a)
E / V vs Hg/HgO/OH$^-$
0.05
0.00
-0.05
-0.10
-0.15
10^0
10^1
10^2
10^3
i_k / mA mg$^{-1}_{Pd}$
Pd/C-AR
Pd/C-300
Pd/C-400
Pd/C-500
Pd/C-600
(b)
E / V vs Hg/HgO/OH$^-$
0.05
0.00
-0.05
-0.10
-0.15
10^{-2}
10^{-1}
10^0
10^1
i_k / mA cm$^{-2}_{Pd}$
Pd/C-AR
Pd/C-300
Pd/C-400
Pd/C-500
Pd/C-600

Figure 6

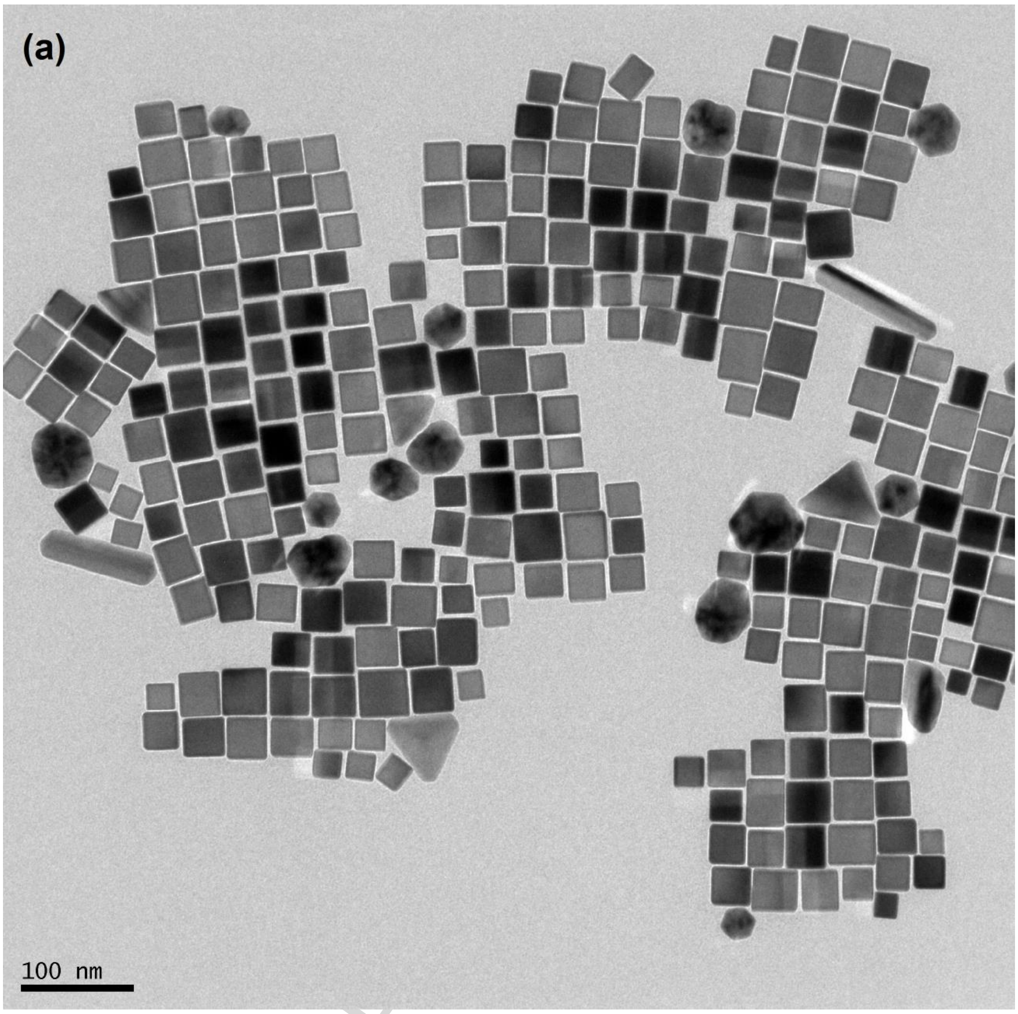

Figure 7a

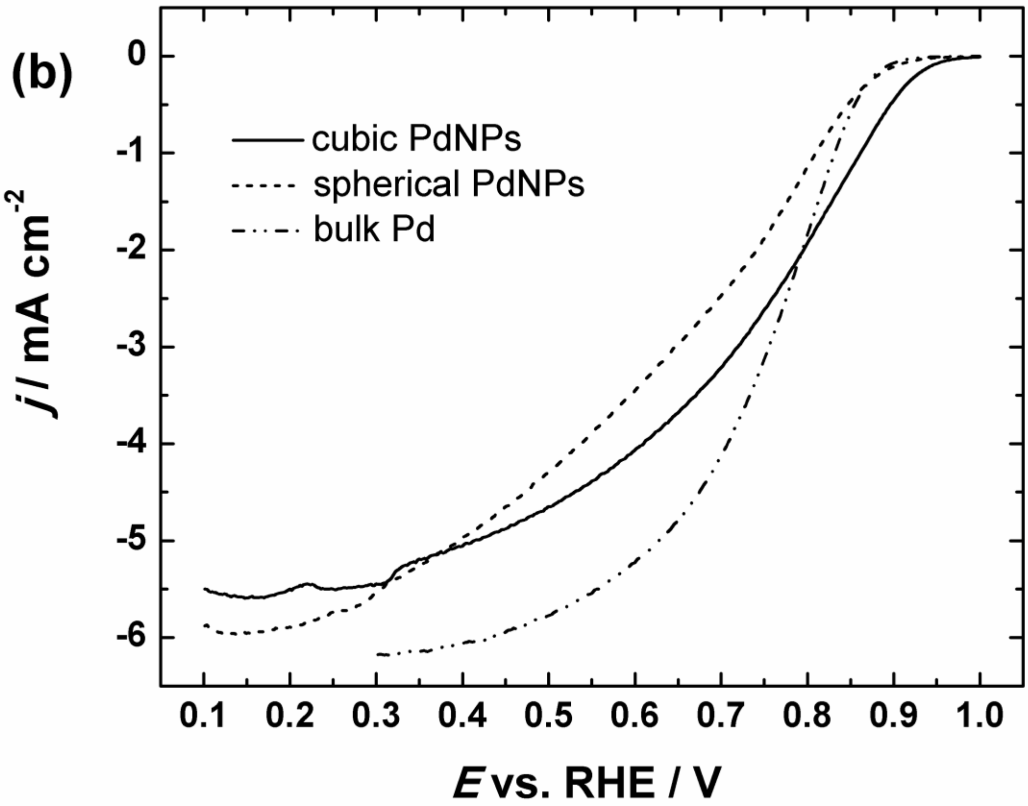
(b)
cubic PdNPs
spherical PdNPs
bulk Pd
j / mA cm^{-2}
0
-1
-2
-3
-4
-5
-6
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
E vs. RHE / V

Figure 7b

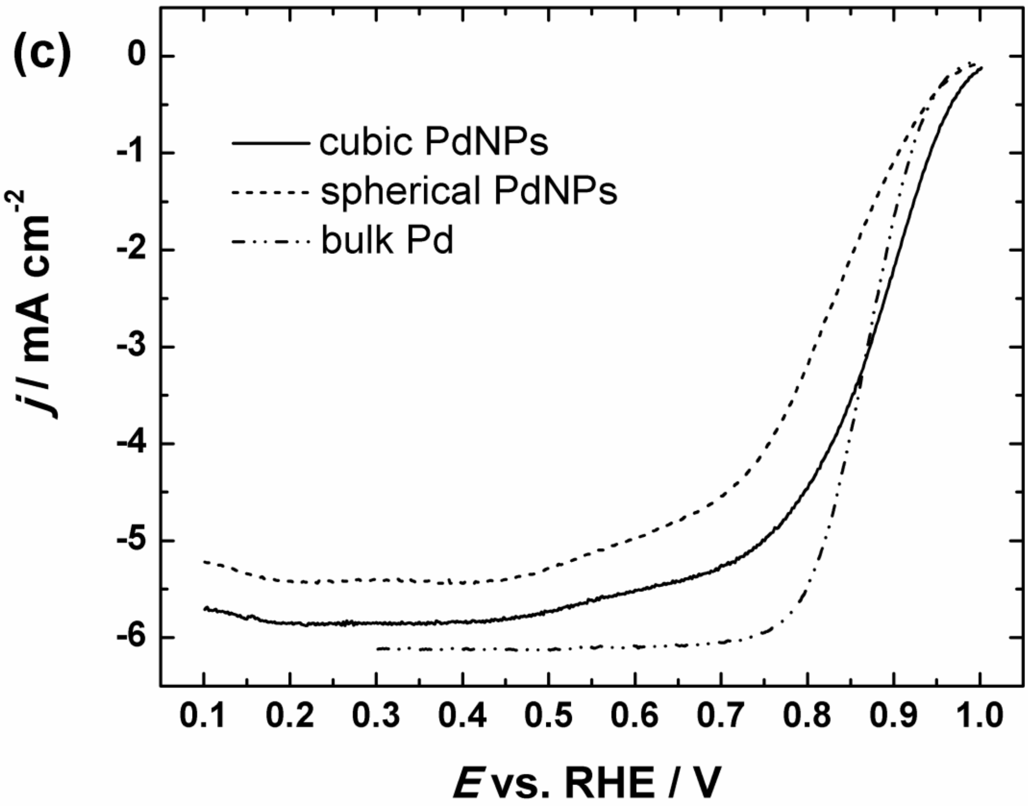
(c)
cubic PdNPs
spherical PdNPs
bulk Pd
0
-1
-2
-3
-4
-5
-6
j / mA cm-2
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
E vs. RHE / V

Figure 7c