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Electroreduction of Oxygen on PdPt Alloy Nanocubes in Alkaline and Acid Media

Kristel Jukk,^[a] Nadezda Kongi,^[a] Kaido Tammeveski,^{[a]*} Jose Solla-Gullón,^[b] and Juan M. Feliu^[b]

Abstract: The electrochemical kinetic behaviour of the oxygen reduction reaction (ORR) on PdPt alloy nanocubes of various composition is investigated in 0.1 M KOH and 0.1 M HClO₄ solutions adopting the rotating disk electrode (RDE) configuration. The PdPt nanocubes are prepared in the presence of polyvinylpyrrolidone and identified by transmission electron microscopy (TEM). TEM micrographs reveal that the PdPt alloy nanoparticles have preferential cubic-shape and the average particle size is ca. 8-10 nm. CO-stripping and cyclic voltammetry (CV) experiments are used for electrochemical cleaning and characterisation of metal nanoparticles. The CV responses indicate alloy formation. In acid media, Pd₃₆Pt₆₄ shows the highest specific activity (SA) for ORR from the alloyed catalysts studied, but this activity is similar to that found with Pt and Pd nanocubes. However, in alkaline solution, the SA value for Pd₇₂Pt₂₈ is about two times higher than that of Pd and Pt nanocubes. The mechanistic pathway of O₂ reduction on PdPt alloy nanocubes is analogous to that of pure Pd and Pt catalysts and the ORR proceeds via a 4-electron pathway in both electrolyte solutions.

1. Introduction

Platinum-based materials are commonly used as cathode electrocatalysts in low-temperature fuel cells.^[1] Although platinum (Pt) is the most active monometallic catalyst for oxygen reduction reaction (ORR), the widespread use of Pt is constrained by its high price and limited availability.^[2] This is the main reason, why many studies have been aimed to find a way to reduce the amount of Pt in fuel cell cathodes. An attractive approach to decrease Pt content in the catalysts is to replace it in part with other metals.^[3] The higher ORR activity of Pt alloys than that of pure Pt is primarily caused by strain and electronic effects. The introduction of other metal compositions not only lowers the content of the precious Pt, but also has an effect on the crystallographic structure and electronic properties of Pt.^[4] In particular, palladium is known for its ability to improve the O₂ reduction activity and durability of platinum.^[5] The properties of Pt and Pd are lot alike (e.g. same group in the periodic table and crystallographic structure, comparable atomic size).^[2, 6] These and also the fact that palladium is cheaper and more abundant

on the Earth's crust make Pd a good substitute for platinum.

The electroreduction of O₂ on Pt and Pd is a structure-affected process and the ORR activity essentially depends on the strength of structure-sensitive anion adsorption on the (hkl) facets. Markovic and colleagues studied O₂ reduction on Pt(hkl) electrodes in perchloric acid and potassium hydroxide solutions.^[7] They found that in alkaline media the ORR electrocatalytic activity decreases in the order Pt(111) > Pt(110) > Pt(100), while in 0.1 M HClO₄, it follows the order of Pt(110) > Pt(111) > Pt(100). Kondo et al. explored the ORR kinetics on Pd low-index planes in 0.1 M HClO₄ and observed that the ORR activity on Pd(hkl) single-crystal electrodes increases in the following order: Pd(110) < Pd(111) << Pd(100).^[8] The specific activity of Pd(100) for O₂ reduction was found to be about 3-times that of Pt(110), the most active single-crystal plane of Pt. In this regard, the O₂ reduction studies on Pd nanocubes in basic media showed an enhancement in the ORR activity as compared to that of Pd spheres, which is in agreement with the domination of Pd(100) facets on the Pd nanocubes.^[9, 10]

Control of the shape and/or composition is highly favourable for the synthesis of novel Pt-based nanostructures with improved activity and utilisation of platinum.^[11, 12] In recent years, several researches have been focused on the preparation of shape-controlled Pt-Pd nanoalloys for electrocatalytic application: nanodendrites,^[13-15] nanoflowers,^[14, 16] concave particles,^[5, 14, 17-19] nanowires and nanorods,^[20-22] polyhedral and octahedral shapes,^[23] nanocubes,^[14, 24-26] etc. Lim et al. prepared Pd-Pt bimetallic nanodendrites as ORR electrocatalysts.^[13] Pd-Pt nanodendrites had 3 times greater specific activity for O₂ reduction than that of the Pt/C catalyst, which has been assigned to the preferable adsorption of O₂ molecules on the stepped facets. Wang and co-workers synthesised Pt-Pd nanoflowers with a simple one-pot method.^[16] These nanocatalysts showed enhanced electrocatalytic ORR performances as compared to commercially available Pd/C and Pt/C catalysts, which could be due to unique structures of Pt-Pd nanoflowers and bimetallic synergistic effects between these precious metals. These authors also prepared Pt-Pd nanocubes anchored to reduced graphene oxide, which were found to exhibit improved ORR activity and stability compared with commercial 10 wt% Pt/C.^[24] Lu et al. prepared PtPd porous nanorods as cathode catalysts for O₂ electroreduction.^[21] These as-prepared nanostructures showed large electroactive surface areas, thus providing an efficient way to reduce the usage of expensive noble metals and, due to the large surface area and the synergy of crystalline alloy phase, the resulting porous nanorods exhibited enhanced electrocatalytic activity for O₂ reduction reaction compared to the commercial Pt/C catalyst. PtPd nanorods showed also excellent durability in the electroreduction of O₂, with only about 6% loss of the initial surface area. Simple one-pot hydrothermal method of synthesis of ultrathin Pd-Pt alloy nanowires was reported by Wu et al.^[22] The Pd-Pt nanowires remarkably outperformed the commercially

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available Pd/C and Pt/C catalysts. The enhanced ORR electrocatalytic activity was explained by the interactions between the Pd and Pt metals and structure peculiarity.

Several research groups have prepared core-shell type Pd-Pt catalysts.^[27-33] Pt monolayer-decorated Pd nanoparticles showed higher ORR activity and stability than Pt/C catalysts.^[27] The activity of PdPt alloy nanoparticles was similar to that of Pd(core)-Pt(shell) catalysts in HClO₄.^[28] Gong et al. synthesised Pt monolayer shell-Pd tetrahedral core electrocatalysts and studied their electrochemical performance towards the ORR in 0.1 M HClO₄ solution.^[29] They found that the half-wave potential increased by 120 mV for the CO-treated Pd-Pt core-shell catalyst compared with non-CO-treated material. Zhang et al. synthesised Pd@Pt core-shell materials with different Pt/Pd molar ratios and studied the electroreduction of O₂ on those catalysts in perchloric acid.^[30] Pd@Pt materials showed enhanced specific activity for O₂ reduction as compared to commercial 20% Pt/C catalyst, the enhancement of the activity was assigned to a weaker adsorption of the intermediate products (OH_{ad}) of the ORR. Shao et al. explored O₂ reduction on Pt shells deposited on shape-controlled Pd nanoparticle cores and detected that the surface structure has strong influence on the ORR activities of Pt shells.^[32] The platinum shells on Pd octahedra had 28 times higher specific activity for O₂ reduction than Pd octahedra due to the weaker oxygen binding energy. Lee et al. established a method for the preparation of truncated Pd nanocubes and their further coating with multi-armed Pt shells.^[33, 34] These Pd-Pt core-shell nanomaterials were employed for ORR electrocatalysis in alkaline media. Pd-Pt nanocubes and Pd nanocubes displayed greater mass activity than Pt nanoparticles, its greater activity was associated to the better accessibility of Pd(100) planes. In previous work, we studied PdPt alloy nanocubes for ORR in 0.5 M H₂SO₄ solution.^[35] PdPt nanocubes manifested increased ORR activity as compared to cubic Pd nanoparticles. In the present study, PdPt nanocubes with various Pd/Pt ratios are investigated as catalysts for O₂ electroreduction in 0.1 M KOH as well as in 0.1 M HClO₄ solutions using the RDE method.

2. Results and Discussion

2.1. Surface morphology and composition analysis

The transmission electron microscopy (TEM) imaging analysis was carried out to obtain knowledge about the particle size and morphology of PdPt alloy nanoparticles. Figs. 1a-c show PdPt nanoparticles with preferential cubic particle shape. Most of the PdPt nanoparticles were cubic-shaped, but there were also observed some truncated particles.

To determine the particle size of PdPt nanocubes, 200 isolated particles were measured. The mean particle sizes were 8.6 ± 0.9 , 9.4 ± 1.4 and 10.4 ± 1.2 nm for Pd₃₄Pt₆₆, Pd₅₀Pt₅₀ and Pd₆₆Pt₃₄ samples, respectively. Particle size distributions for all the alloyed catalysts are shown in Fig. 1. The average particle sizes of Pd and Pt nanocubes were about 10 nm.

The composition of the prepared PdPt alloy nanocubes was analysed by energy dispersive X-ray spectroscopy (EDS). The

EDS analyses displayed that the atomic compositions were close to the nominal values and the Pd-to-Pt ratios of 36:64, 54:46 and 72:28 were determined.

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging and EDS elemental mapping experiments were performed in order to investigate the elemental composition and distribution of PdPt nanocubes (Fig. 2). It is clearly seen from the elemental mapping images (Fig. 2b,c) that Pd and Pt metals are homogeneously distributed throughout the nanoalloy structure.

2.2. Electrochemical characterisation of PdPt alloy nanocubes

In order to clean the PdPt alloy nanocubes electrochemically without changing the initial nanostructure of the catalysts, CO adsorption and its subsequent electrochemical oxidation was used.^[36] Typical CO-stripping behaviour in 0.1 M KOH and 0.1 M HClO₄ solutions is shown in Fig. 3. In both solutions, it can be seen that there is a positive potential shift in the position of the CO oxidation peak of PdPt alloys with rising the amount of Pd. A similar tendency was also observed previously in 0.5 M H₂SO₄ solution and it has been proposed to be related to a gradual Pd surface enrichment for increasing Pd content.^[35, 37]

After CO-stripping experiments, representative cyclic voltammograms (CV) can be obtained as shown in Figs. 4a,b. The CV responses in both solutions displayed improvement in surface cleanliness as compared to the initial ones (before CO adsorption and stripping). Characteristic hydrogen adsorption/desorption region is in evidence for all the PdPt alloy nanocubes studied. In alkaline solution distinctive peaks of underpotential deposited hydrogen (H_{upd}) of Pt for palladium-rich alloys are not well-defined, but with increasing Pt content these peaks are more pronounced. These characteristic peaks for Pd₃₆Pt₆₄ catalyst are observed at potentials of about 0.28 and 0.40 V, but for Pd₅₄Pt₄₆ these peaks shifted to more negative potentials (0.26 and 0.37 V), and for Pd₇₂Pt₂₈ alloy only one peak appears at 0.25 V. Lee et al. reported similar CV response for Pd-Pt core-shell nanocubes.^[33] The differences in the CV curves in the perchloric acid solution are smaller and this kind of conclusions could not be reached. For comparison reasons the stable CVs of cubic Pd and Pt nanoparticles are added to Figs. 4a,b. The values of real electrochemically active surface area (*A_r*) were determined for all catalysts and are listed in Tables 1 and 2.

2.3. Oxygen reduction in 0.1 M KOH solution

The O₂ reduction reaction on cubic PdPt nanoalloys was explored in oxygen-saturated 0.1 M potassium hydroxide solution using the rotating disk electrode (RDE) technique. Fig. 5a presents characteristic current density-potential (*j*-*E*) curves for the Pd₅₄Pt₄₆-catalyst. The background currents, measured in the same conditions (10 mV s⁻¹, potential region between 0.05 and 1.05 V) in deaerated solution, were subtracted from the oxygen reduction currents. Only the anodic sweeps are shown and further analysed. Single-wave ORR polarisation curves with well-developed diffusion-limited current plateaux were noticed for all the PdPt electrocatalysts studied.

To calculate the electron transfer number (n) the Koutecky-Levich (K-L) equation was used:^[38]

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_d} = -\frac{1}{nFkC_{O_2}^b} - \frac{1}{0.62nFD_{O_2}^{2/3}\nu^{-1/6}C_{O_2}^b\omega^{1/2}} \quad (1)$$

where j is the experimentally measured current density at a specific potential E , j_k is the kinetically controlled current density at E and j_d is the diffusion-limited current density, k is the rate constant for O_2 electroreduction at E , F is the Faraday constant ($96,485 \text{ C mol}^{-1}$), ω is the rotation rate of the electrode (rad s^{-1}), $C_{O_2}^b$ is the solubility of O_2 in 0.1 M KOH ($1.2 \times 10^{-6} \text{ mol cm}^{-3}$),^[39] D_{O_2} is the diffusion coefficient of O_2 in 0.1 M KOH solution ($1.9 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)^[39] and ν is the kinematic viscosity of the electrolyte solution ($0.01 \text{ cm}^2 \text{ s}^{-1}$).^[40] The Koutecky-Levich

analysis results for $\text{Pd}_{54}\text{Pt}_{46}$ alloy nanocube-modified electrode are presented in Fig. 5b. Linear K-L plots were acquired from the rotating disk electrode data. The n value was determined from the slope of the K-L lines and it was about four for all the electrodes studied (inset to Fig. 5b). The 4-electron O_2 reduction mechanistic pathway on Pd and Pt catalysts in alkaline media has been also obtained in previous studies,^[24, 33, 41, 42] however, it has been suggested that on Pt-group metals the ORR occurs partly via 2-electron pathway.^[43] Lee et al. suggested that the ORR kinetic properties on Pt-coated Pd nanocubes are better than on Pt nanoparticles and as a result the production of HO_2^- is lower.^[33]

Figure 1. TEM images of PdPt electrocatalysts: (a) $\text{Pd}_{36}\text{Pt}_{64}$, (b) $\text{Pd}_{54}\text{Pt}_{46}$ and (c) $\text{Pd}_{72}\text{Pt}_{28}$ and their corresponding particles size histogram.

Figure 2. HAADF-STEM image (a) and EDS elemental maps of Pd (b) and Pt (c) for Pd₃₆Pt₆₄ catalyst material.

Figure 3. Electro-oxidation of preadsorbed CO on PdPt catalysts, Pd and Pt nanocubes in Ar-saturated (a) 0.1 M KOH and (b) 0.1 M HClO₄ solutions ($v = 20 \text{ mV s}^{-1}$). Current densities are normalised to the real surface area of electrocatalysts.

A direct comparison of the RDE results of O₂ reduction recorded at 1900 rpm is presented in Fig. 6a. It can be seen that all the cubic-shaped nanocatalysts show similar electrochemical ORR behaviour displaying two distinct regions of mass-transfer (below 0.7 V) and mixed kinetic-diffusion control in the region of potentials between 0.7 and 1.0 V. The half-wave potential ($E_{1/2}$) values for all the electrocatalysts studied are listed in Table 1. Pd₃₆Pt₆₄ and pure Pt nanocubes had slightly lower $E_{1/2}$ for O₂ reduction than the other catalysts in this study. Lower electrocatalytic activity could be explained by higher Pt(100) content, which is the least active facet for ORR in alkaline media.^[7]

Figure 4. Cyclic voltammograms recorded after CO oxidation on PdPt catalysts, Pd and Pt nanocubes in Ar-saturated (a) 0.1 M KOH and (b) 0.1 M HClO₄ solutions ($\nu = 50 \text{ mV s}^{-1}$). Current densities are normalised to the real surface area of electrocatalysts.

Tafel plots (Fig. 6b) were constructed using the RDE data (shown in Fig. 6a) of O₂ reduction at 1900 rpm. Two characteristic regions in Tafel plots with distinct slope values were found. At low current densities the slope value was approximately -60 mV dec^{-1} and in the region of higher current densities the Tafel slope increased to -120 mV dec^{-1} . Similar Tafel behaviour for O₂ electroreduction has been reported in earlier works.^[9, 42]

Figure 5. (a) RDE polarisation curves for oxygen reduction on Pd₅₄Pt₄₆ alloy nanocubes in O₂-saturated 0.1 M KOH ($\nu = 10 \text{ mV s}^{-1}$). (b) K-L plots for ORR in 0.1 M KOH (inset shows the potential dependence of n). Current densities are normalised to the geometric area of GC.

Specific activity (SA) for O₂ reduction on the catalysts was calculated by following equation:

$$SA = I_k / A_r \quad (2)$$

where I_k is the kinetic current at a specific potential and A_r is the real electroactive surface area. The SA values calculated at 0.9 V are listed in Table 1. Specific activity for PdPt alloy nanocubes increased with increasing Pd content. Interestingly, the SA values for Pd₇₂Pt₂₈ and Pd₅₄Pt₄₆ alloys are 1.249 and 0.622 mA cm⁻², respectively. Thus, the SA for Pd₇₂Pt₂₈ is about 2-times higher than that obtained with pure Pd and Pt nanocubes (about 0.55–0.6 mA cm⁻²) indicating a bimetallic synergetic effect between Pd and Pt at this particular composition. In this regard, it has been found that an insignificant amount of Pt on top of the Pd nanotubes improves the ORR activity in alkaline media.^[44] The enhancement of the specific and mass activities for ORR was attributed to electronic effects and higher surface area utilisation.

Figure 6. (a) Comparison of the RDE results for O₂ reduction on PdPt, Pd and Pt nanocubes in O₂-saturated 0.1 M KOH ($\nu = 10 \text{ mV s}^{-1}$, $\omega = 1900 \text{ rpm}$) and (b) Tafel plots for ORR in 0.1 M KOH ($\omega = 1900 \text{ rpm}$). Current densities are normalised to the geometric area of GC.

Table 1. Kinetic parameters for oxygen reduction on different nanocubes in O₂-saturated 0.1 M KOH, $\omega = 1900 \text{ rpm}$.

Electrode	Ar (cm ²)	Tafel slope (V dec ⁻¹) I region ^[a]	Tafel slope (V dec ⁻¹) II region ^[a]	$E_{1/2}$ (V)	SA at 0.9 V (mA cm ⁻²)
Pd ₃₆ Pt ₆₄	0.44	-0.059	-0.119	0.86	0.375
Pd ₅₄ Pt ₄₆	0.49	-0.059	-0.114	0.89	0.622
Pd ₇₂ Pt ₂₈	0.32	-0.060	-0.126	0.89	1.249
Cubic Pd	0.52	-0.056	-0.122	0.89	0.607
Cubic Pt	0.31	-0.061	-0.121	0.87	0.544

[a] Region I corresponds to low current densities and Region II to high current densities.

2.4. Oxygen reduction in 0.1 M HClO₄ solution

Oxygen electroreduction on PdPt catalysts was also studied in O₂-saturated 0.1 M HClO₄ solution using the RDE setup. Typical RDE voltammetry curves for O₂ electroreduction on Pd₅₄Pt₄₆ nanocubes are demonstrated in Fig. 7a. The ORR polarisation curves showing a single reduction wave were in evidence for all the electrocatalysts studied in the present work.

The RDE data were analysed using the K-L equation (Eq. (1)), where the values of oxygen solubility ($C_{O_2}^b = 1.26 \times 10^{-6} \text{ mol cm}^{-3}$)^[45] and diffusion coefficient ($D_{O_2} = 1.93 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$)^[45] were utilised for 0.1 M HClO₄ solution. Linear K-L plots for O₂ reduction were obtained from the RDE data (Fig. 7b).

From the K-L slopes the value of n was calculated, which was close to four over the whole range of potentials for all the electrocatalysts studied (see inset in Fig. 7b). This suggests that the main product of the ORR is water and only little peroxide is formed. On hollow Pd-Pt nanostructures using the rotating ring-disk electrode method the H₂O₂ yield was found to be <0.15%.^[5] The 4e⁻ pathway of O₂ electroreduction on Pd and Pt electrocatalysts in acid media has been also confirmed in earlier studies.^[21, 25, 46]

A comparison of the RDE results in perchloric acid at 1900 rpm is shown in Fig. 8a. Pd₃₆Pt₆₄ had the highest half-wave potential from the alloys; its $E_{1/2}$ value was comparable with that of pure Pt nanocubes (Table 2). Similar $E_{1/2}$ values have been also found for PdPt nanodendrites.^[15, 25] GC electrodes modified with Pd₅₄Pt₄₆ and Pd₇₂Pt₂₈ nanocubes had the lowest $E_{1/2}$ (0.83 and 0.84 V, respectively), which were similar to that of cubic Pd nanoparticles ($E_{1/2} = 0.84 \text{ V}$). Although Pd(100) is recognised to be the most active single-crystal facet for ORR in 0.1 M HClO₄ solution,^[8] the alloy nanocubes with more than 50% Pd had lower electrocatalytic activity towards O₂ reduction. The reason for this observation might be that there are more Pd(110) or Pd(111) sites, which are less electrocatalytically active for ORR than Pd(100), available on the surfaces of Pd₅₄Pt₄₆ and Pd₇₂Pt₂₈ nanocubes as Fig. 1 suggests. Similar results were found also by Zhang et al., who demonstrated that Pd-Pt bimetallic nanocrystals had lower O₂ reduction activity than commercial Pt/C catalyst.^[17]

It has been reported that the addition of defects leads to a remarkable diminution of the electrocatalytic activity for ORR on Pt(111) surfaces,^[47] but there is still lack of knowledge about the role of defects on Pt(100) facets.^[48] Quan et al. have observed that the specific activity towards the O₂ reduction reaction on (720)-bounded Pt concave nanocubes was greater than that of low-indexed Pt nanocubes with similar size.^[49] Ma et al. studied the ORR on Pt multicubes and Pt multipods.^[50] They found that Pt multicubes are surrounded largely by (100) facets, in contrast to the Pt multipods, which have high-index facets, but still exhibit an increased $E_{1/2}$ value (0.955 and 0.957 V for Pt multicubes and Pt multipods, respectively) and high specific activities (0.729 mA cm⁻² for multicubes and 0.924 mA cm⁻² for multipods). In case of Pd concave nanocubes with (730) high-index facets, it has been found that these exhibit enhanced electrocatalytic properties for formic acid electro-oxidation compared to the conventional Pd nanocubes enclosed by (100) low-index

facets.^[51] It is still not clear how the high-index facets affect the ORR activity of Pd single crystal basal planes.

Tafel plots were derived from the RDE data of O₂ reduction (shown in Fig. 8a) and two Tafel regions with different slope value were observed (Fig. 8b). In the potential region of low current densities the Tafel slope is close to -60 mV dec⁻¹ and in the region of higher current densities the slope values increase over -120 mV dec⁻¹. These Tafel slopes are characteristic to both of the noble metal electrocatalysts studied, Pd and Pt, and the change in the slope is associated with the potential-dependent coverage of oxygen-containing species that inhibit the adsorption of O₂.^[52] For ORR the main barrier for the rate-determining step was identified as the structure-sensitive adsorption of OH species and its inhibiting effect on O₂ adsorption.^[53] For pure Pt electrocatalysts Pt-OH is easily formed on the surface of platinum, thus lowering the ORR activity.^[54] In comparison with that of pure Pt, the addition of palladium into the Pd-Pt catalysts showed that the degree of Pt-OH appeared on the surface of Pd@Pt is decreased and therefore enhances the activity of O₂ reduction. Similar observation of low OH_{ad} coverage on the surface of Pt-on-Pd has been made by Peng and Yang.^[55] The electrocatalytic ORR activity of the hetero-nanostructures increased nearly two times.

Table 2. Kinetic parameters for oxygen reduction on different nanocubes in O₂-saturated 0.1 M HClO₄, ω = 1900 rpm.

Electrode	A _r (cm ²)	Tafel slope (V dec ⁻¹) I region ^[a]	Tafel slope (V dec ⁻¹) II region ^[a]	E _{1/2} (V)	SA at 0.9 V (mA cm ⁻²)
Pd ₃₆ Pt ₆₄	0.61	-0.062	-0.128	0.88	0.408
Pd ₅₄ Pt ₄₆	0.59	-0.059	-0.126	0.83	0.241
Pd ₇₂ Pt ₂₈	0.65	-0.060	-0.128	0.84	0.216
Cubic Pd	0.41	-0.059	-0.121	0.84	0.249
Cubic Pt	0.73	-0.063	-0.124	0.89	0.416

[a] Region I corresponds to low current densities and Region II to high current densities.

The specific activities for O₂ reduction were also calculated in 0.1 M HClO₄ solution. The SA values were determined using Eq. (2) and are presented in Table 2. In acid media, the specific activities at 0.9 V vs. RHE were lower as compared to those determined in alkaline solution and the order of the SA values for PdPt alloy nanocubes in 0.1 M HClO₄ is adverse to that observed in 0.1 M KOH solution. In perchloric acid Pd₃₆Pt₆₄ nanocubes demonstrated the highest SA value (0.408 mA cm⁻²) from the alloyed catalysts and it was comparable to that of pure Pt nanocubes (0.416 mA cm⁻²). This nanoalloy with highest Pt content exhibited good ORR activity also in sulphuric acid in our previous work.^[35] It has been reported that Pd-Pt concave nanocubes exhibited high electrocatalytic activity for O₂ electroreduction.^[18] Enhanced ORR activity was interpreted by

higher Pt concentration on the surface of the Pd nanoparticles and also the electronic synergy between Pt and Pd could lead to an increased ORR activity. It has been found for Pd-Pt core-shell systems that the Pd/Pt ratio has a major effect on the activity of O₂ reduction reaction.^[54] Compared to pure palladium, Pt is more active. With the increase of the Pt/Pd molar ratio, more Pt nanoclusters were formed on the surface of Pd nanocubes, resulting in the enhanced electrocatalytic activity. Liu et al. studied the ORR electrocatalytic activity of conventional PdPt alloy nanoparticles and compared their specific activity with that of Pd(core)-Pt(shell) and Pt/C catalysts.^[28] It was found that in 0.1 M HClO₄ solution the SA for PdPt nanoalloys increased with the increased Pt/Pd ratio. The SA values for O₂ reduction of PdPt alloy nanocrystals were even higher with those of Pd-Pt core-shell catalysts. The electrocatalytic trends observed in the present work in HClO₄ are in good agreement with those results reported for conventional PdPt alloy nanoparticles by Liu et al.^[28] These observations suggest that alloy formation between Pd and Pt may have a large role for the specific activities observed in the present work.

Figure 7. (a) RDE polarisation curves for oxygen reduction on Pd₅₄Pt₄₆ alloy nanocubes in O₂-saturated 0.1 M HClO₄ (ν = 10 mV s⁻¹), (b) K-L plots for ORR in 0.1 M HClO₄ (inset shows the potential dependence of n). Current densities are normalised to the geometric area of GC.

Figure 8. (a) Comparison of the RDE results for O₂ reduction on PdPt, Pd and Pt nanocubes in O₂-saturated 0.1 M HClO₄ ($\nu = 10$ mV s⁻¹, $\omega = 1900$ rpm) and (b) Tafel plots for ORR in 0.1 M HClO₄ ($\omega = 1900$ rpm). Current densities are normalised to the geometric area of GC.

3. Conclusions

PdPt nanocubes were tested as novel electrocatalysts for O₂ reduction reaction in alkaline and acid media. The surface morphology of PdPt alloys was examined by TEM, which displayed cubic-shaped nanoparticles with mean particle size about 8-10 nm. From the EDS analysis the relative content of Pt and Pd metals in the nanoalloys were determined. In alkaline media, the specific activities of the PdPt nanocubes increased with increasing Pd content and Pd₇₂Pt₂₈ catalysts showed the highest specific activity towards the ORR. This SA value represents a twofold ORR activity enhancement in comparison to cubic Pd and Pt nanoparticles. However in perchloric acid, the activity of PdPt nanocubes (independently of their atomic composition) was not found to be improved over the ORR activity of Pt and Pd nanocubes. In this case, the SA value of the alloys increased with increasing Pt content. The electron transfer number in both solutions was close to four. The mechanistic

pathway of the ORR on PdPt alloy nanocubes at low current densities was the same as on cubic Pd and Pt nanoparticles.

Experimental Section

Synthesis of PdPt nanoalloys

Cubic PdPt alloy nanoparticles were prepared using the procedure published earlier.^[11, 35] Different composition of PdPt nanocubes was achieved by varying the amounts of potassium tetrachloropalladate (>99.99%, Sigma-Aldrich) and potassium tetrachloroplatinate (>99.99%, Sigma-Aldrich) in the reaction mixtures. The Pd/Pt ratios were 34/66, 50/50 and 66/34. The alloyed nanocrystals were compared to pure Pd and Pt nanocubes. Cubic Pd nanoparticles were synthesised via the polyvinylpyrrolidone (PVP) method reported elsewhere^[56] and Pt nanocubes were prepared by the water-in-oil microemulsion method.^[57]

Surface characterisation of PdPt nanoalloys

The surface and composition characterisation of the PdPt nanoalloys was carried out using transmission electron microscope (JEOL, JEM-2010) working at 200 kV, assembled with an X-ray detector OXFORD INCA Energy TEM 100 for energy dispersive X-ray spectroscopy analysis. The samples for TEM examination were made by pipetting ethanol/acetone dispersions of the PdPt alloy nanoparticles onto a Formvar-covered copper specimen surface and leaving the solvent to dry in air at room temperature.

HAADF-STEM imaging and EDS elemental mapping was performed in order to investigate the surface structure of prepared catalyst materials. Sample was measured with FEI Titan Themis 200 Cs corrected microscope working at 80 kV. EDS signal was collected with SuperX SDD (Bruker). EDS data was processed with Cliff-Lorimer method.

Electrochemical measurements

Electrochemical measurements were conducted in a conventional glass cell using 3-electrode configuration in 0.1 M KOH and 0.1 M HClO₄ solutions. The experiments were controlled using Autolab PGSTAT128N potentiostat/galvanostat (Metrohm Autolab, The Netherlands) with General Purpose Electrochemical System (GPES) software. A Pt-spring served as a counter electrode and the reversible hydrogen electrode (RHE) was employed as a reference electrode. All the potentials in this study are reported with respect to the RHE.

A glassy carbon electrode ($d = 3$ mm) was used as substrate for different nanoparticles and was purchased from Radiometer (Copenhagen). GC electrodes were polished with 1.0 and 0.3 μ m alumina slurries (Buehler). After polishing, the electrodes were sonicated in Milli-Q water for 5 min. The working electrode surface was modified by dropping 3 μ L of the PdPt catalyst suspension in water on the GC electrode substrate. The nanoparticle-modified electrodes were dried in N₂ flow at room temperature and electrochemically tested after complete solvent evaporation.

The electrolyte solutions were prepared utilising Milli-Q water and KOH pellets (p.a., Sigma-Aldrich) or 70% perchloric acid (Aldrich). Solutions were aerated with pure O₂ (99.999% AGA) or saturated with Ar gas (99.999% AGA). Cyclic voltammetry (CV) experiments were conducted in O₂-free electrolyte solutions at a scan rate (ν) of 0.05 V s⁻¹. CO-stripping examination was used as an ultimate and gentle cleaning method of the

nanostructured catalyst. The electrode potential was kept at 0.05 V (0.1 V for pure Pd nanocubes) while CO gas (99.97%, AGA) was introduced to the electrolyte solution. After saturating with carbon monoxide (1 min), the CO was removed by bubbling Ar through the test solution for at least 30 min at constant potential (0.05 V; 0.1 V for Pd nanocubes). The real electroactive surface area of the PdPt nanoalloy, Pd and Pt nanocubes was calculated using the charge corresponding to hydrogen under potential deposition ($H_{\text{upd}}(\text{Pt}) = 210 \mu\text{C cm}^{-2}$,^[37] and $H_{\text{upd}}(\text{Pd}) = 212 \mu\text{C cm}^{-2}$,^[58]). The A_r for pure Pd nanocubes in 0.1 M KOH solution was determined by integrating the amount of charge under the Pd oxide reduction peak, utilising the value of $424 \mu\text{C cm}^{-2}$ corresponding to the reduction of PdO monolayer.^[59]

Oxygen electroreduction on PdPt nanocatalysts was studied in O₂-saturated 0.1 M KOH and 0.1 M HClO₄ solutions using the rotating disk electrode method at a scan rate of 0.01 V s⁻¹. The electrode rotation rate ($\omega = 360\text{--}4600$ rpm) was applied by an EDI101 rotating device equipped with a CTV101 speed control apparatus (Radiometer, Copenhagen). All the electrochemical experiments were conducted at room temperature (23±1 °C).

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Keywords: PdPt alloy nanocubes • electrocatalysis • oxygen reduction • Pt nanocubes • Pd nanocubes • bimetallic catalysts

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Layout 1:

ARTICLE

PdPt alloy nanocubes of various composition are synthesised and used as electrocatalysts for oxygen reduction reaction (ORR) in 0.1 M KOH and 0.1 M HClO₄ solutions. The size of PdPt nanocubes is 8-10 nm. Different ORR activity trends for cubic PdPt alloy nanoparticles are reported for acidic and alkaline media.

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Electroreduction of Oxygen on PdPt Alloy Nanocubes in Alkaline and Acid Media

Layout 2:

ARTICLE