Tuning the properties of PtPd nanoparticles by varying metal composition and capping agents

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This study demonstrated a rapid method of producing PtPd via chemical reduction by varying metal composition and types of capping agents. The effect of different compositions between the two-metal precursor, Pt and Pd, is invested by tuning at various volume ratios of 3:1, 1:3, and 1:1 and comparing them with their single counterparts. The FESEM results show that all prepared samples exhibit nanosponges structure. PtPd of 1:1 ratio has the highest ECSA of 14.25 m²/g, while PtPd with PVP exhibits a high ECSA value of 692.7 m²/g compared to those without capping agent (287.8 m²/g), indicating large active sites, which increases its catalytic function.

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1. Introduction

As urbanisation and industrialisation continue to grow, global energy demand is increasing exponentially. This puts a strain on our environment, as we rely more heavily on fossil fuels. Shifting to renewable energy sources is more important than ever to reduce our dependence on fossil fuels and protect the planet. By adopting green energy sources, we can help to alleviate the effects of climate change and create a clean, sustainable, and affordable energy future for all. As we strive to create a sustainable future with alternative power sources, fuel cells are emerging as a clean and efficient way to fight climate change. One of the most viable candidates for alternative power sources is the direct methanol fuel cell (DMFC) applicable to a wide range of portable, mobile electronics and wearable devices [1]. Compared to other power sources such as hydropower and nuclear reactors, DMFCs have numerous advantages, including lower weight and size, conveying clean energy, and less pollution. Most importantly, DMFC has high energy density and low operating temperature and has been rated as the most favoured portable energy device to replace lithium batteries. DMFC exhibit a theoretical energy density of 15 times greater than the lithium-ion battery, and their replenishment is quickly achieved by refilling the fuel cartridge within seconds [2]. Despite these advantages, DMFCs encounter some drawbacks that limit their efficiency such as sluggish kinetics methanol oxidation reactions (MOR), methanol cross-over through the polymer electrolyte membrane, and the high price of the whole device [3-5]. These limitations must be solved for DMFC to be commercialised.

The selection of noble metal catalysts at the anode and cathode exhibits a crucial impact on DMFC performances and the cost of the DMFC. Platinum (Pt) is often used as a benchmark catalyst for MOR and oxygen reduction reaction (ORR) due to its high catalytic performance toward electrooxidation of small organic fuels on the anode and oxygen reduction on the cathode, outstanding chemical resilience, corrosion resistance and high melting point. However, it has a drawback. At the cathode compartment, it tends to promote methanol oxidation during ORR, resulting in mixed potential, and reducing the overall cell voltage [6]. Additionally, Pt can easily be poisoned by the strong adsorption of carbon monoxide (CO) molecules produced by small

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molecules of organic fuel oxidation, resulting in a deactivating catalytic process [7,8]. Several approaches of the last decade were explored with the aim of reducing cost and improve MOR performance.

Alloying Pt with other noble metals such as Pd, Au, Ag, or 3d transition metals like Fe, Ni, Co, and Cu has been reported to improves MOR and ORR's activity compared to Pt alone due to electronic (i.e., increased Pt d-band vacancy) and geometric effects (i.e., optimized Pt-Pt interatomic distance) [9]. Alloying causes lattice contraction, which results in a more favourable Pt–Pt distance for O_2 adsorption [10]. Pd is the most favoured alloy with Pt as it can reduce protons, store, and release hydrogen. It is also able to remove adsorbed CO formed from the methanol electrooxidation, thus lessening the poisoning effect [11]. Mahapatra and Datta reported that the Pd could release hydrogen and this hydrogen able to provide a route for lowering the surface concentration of adsorbed CO, enabling the continual oxidation of organic molecules at the Pd surface. Alloying Pd with Pt will alter the electronic structures of Pt, thereby reduce poisoning by oxidizing CO to CO₂ [11]. Additionally, because the atomic radius of Pt and Pd are similar (0.138 and 0.137 nm), replacing Pt with Pd atoms only slightly increases the lattice, and both discovered to have the face centred cubic structure [11]. Despite all the merits, Pd is less studied for fuel cell applications compared to Pt. Nanostructure materials are made up of a few hundred to a few thousand atoms with a high surface-to-volume ratio. They exhibit unique and novel properties that are different from their bulk counterpart. Nanostructure material is advantageous in heterogeneous catalysis because reactions can occur on the catalyst surface. Particle size and shape significantly impact nanoparticle catalytic properties; small particles have a large surface area, whereas faceted (low index, high index, and complex) shapes boost catalytic performance. Understanding the structure-properties relationship is crucial in developing an efficient catalyst.

The last decades have witnessed the preparation of PtPd alloy with different shapes such as wires [11-13], icosahedral [14], tetrahedral [15], dendrites [16], clusters [17], octahedral [18] and cubes [19]. For example, Zhang and his co-workers prepared PtPd alloys with selective shapes by a one pot solvothermal method [20]. Lim et al. synthesized Pt-Pd nanodendrites using Pd nanoparticles as seeds [21]. Among the structures, porous architectures such as nanosponges outshine the others as they have unique characteristics of their own n [22]. They have gained considerable interest in catalysis field due to high surface area, low density, higher mass transfer and electron mobility. This characteristic is desirable in catalysis as reactions can take place on the surface of catalyst [23]. To date, great efforts are being put towards the synthesis of porous structures such as seed meditated growth, dealloying approaches [24], carbothermal methods [25] and sol-gel approaches [26]. Nevertheless, the above methods suffer from relatively high cost, needing complex steps and rigorous operation skills. Most of the synthesis requires a capping agent or surfactant to stabilise and shaping the structures. However, these capping agents and surfactants tend to adsorb on the active sites of the metal and reduce the efficiency of the catalyst Therefore, a simple and cheap method of preparing of PtPd to perform redox reaction. nanostructures is highly desirable. Among the techniques, chemical reduction method is a simple and rapid. It requires a reducing agent to reduce the chemical reactants in either aqueous or nonaqueous solvents. This approach allows for mass and rapid production, controlling the nanoparticles' size, structure, and shape compared to other techniques. This work focused on the synthesis of PtPd bimetallic alloys nanoparticles using a simple, rapid, one step reduction method by tuning Pt and Pd compositions at (1:1, 1:3 and 3:1) ratio. The best ratio will be used for further analysis on the effect of capping agents (i.e polyvinylpyrrolidone (PVP), polyvinyl alcohol (PVA) and polyethylene glycol (PEG)) on the morphological structural, and catalytic activities toward methanol electrooxidation. The produced PtPd nanoparticles will be assessed using X-ray diffraction (XRD) for structural analysis, Field Emission Scanning Electron Microscopy (FESEM) for morphological studies and cyclic voltammetry measurements to investigate their performances of methanol oxidation reaction.

2. Methodology

All the chemical substances were high-analytical reagents and used without further purification. Sodium borohydride (NaBH₄), Chloropalladaic acid (H₂PdCl₄) and Chloroplatinic acid (H₂PtCl₆) were obtained from Sigma Aldrich. The protocol for preparation of PtPd nanoparticles consists of several steps. Firstly, the Pd metal precursor H₂PdCl₄ (2.5 mL,0.1 M) was prepared by mixing Palladium (II) Chloride (PdCl₂) and Hydrochloric acid (HCl) in 50 mL deionized water. Then 1 mL of the solutions H_2PdCl_4 and H_2PtCl_6 (2.5 mL,0.1 M) were quickly injected into 10 mL NaBH₄ (2.5 mL,0.1 M) at room temperature. The mixture was stirred for 5 min. Then, the solution was centrifuged at 8000 rpm and washed with deionized (DI) water for a few times to remove the unwanted product. Finally, the PtPd was re-dispersed in DI water for characterization. The same procedure was repeated with various composition of Pd:Pt ratios (3:1, 1:3) and compare with monometallic Pd and Pt with all conditions kept the same. Next, 0.1 g of PVP (MW= 40000) was added to the best ratio and served as the capping agent. The PVP was replaced with PVA and PEG (PEG 400) with the parameters kept the same. Finally, the product was centrifuged, washed with DI water, and redisperse before characterization. For XRD analysis, the samples were prepared by drop-casting the PtPd suspension on glass substrates and dried at 60 ^oC. The process was repeated several times to form layers of thick film. Prior to the drop-casting process, the glass substrates were cleaned using an aqua regia solution and rinsed with distilled water. The structural properties were analyzed using XRD diffractometer employing Bruker D8 Advance at a scanning rate of 0.05° per step with 2 Θ ranging from 40 to 90 using monochromatic Cuk α radiation (1.5418 Å). For FESFEM analysis, the samples were prepared by pipetting the PtPd suspension on a top of silicon wafer and left to dry at room temperature. The morphology of the samples was characterized using FESEM (NOVA Nanosem 45) working at the acceleration voltage of 5 kV. The synthesized samples were tested for methanol oxidation using an eDAQ (ER466) Integrated Potentiostat with a three-electrode cell consisting of Ag/AgCl as a reference electrode, Platinum rod as an auxiliary electrode, and glassy carbon as a working electrode. A 5 μ L of PtPd sample (with a loading of 10 μ g) was drop-casting on a glassy carbon electrode ($\phi =$ 3.0 mm, surface area 0.07 cm²). Prior to that, the glassy carbon was polished with α -Al₂O₃ (0.3 μ m and 0.05 μ m), rinsed with DI water and dried with N₂ flow. Once PtPd has dried on the glassy carbon, a 5 µL Nafion® solution was dropped onto the PtPd film and allowed to dry at room temperature. Throughout the measurements, the electrolytes for electrochemical testing were deaerated with high purity of N₂ gas. Analysis of Pt-O and Pd-O reduction process was performed using cyclic voltammetry (CV) in 10 mL of 1 M KOH electrolyte, with a potential sweep rate of 50 mV/s and a scanning potential between -0.8 V to 0.4 V vs. Ag/AgCl. The oxidation of methanol was studied for 20 cycles by adding 10 mL of 1 M MetOH in the alkaline solution at -0.8 V and 0.8 V vs. Ag/AgCl.

3. Results and discussions

All syntheses behave in a consistent manner during the experiment. The yellowish solutions instantly transform into black dispersions upon adding the reducing agent, i.e., NaBH₄. The observations suggest the synproportionation of hydride ions and protons, and the formation of reduced metal species. The black dispersion solution agglomerated quickly and forms black precipitate for all the synthesised samples. The FESEM results for the Pt:Pd samples produced at the volume ratio of 1:1,1:3,3:1 and the monometallic Pd and Pt are shown in Fig.1. Note that no additional capping agent was used during the whole process. At 100k times magnification (scale: 500 nm), it is observed that all samples are composed of open interconnected network backbone with several small pores embedded within it, forming nanosponges structures. The largest pore size diameter of 5.6 nm is obtained from the PtPd sample with volume ratio of 3:1. Meanwhile, the smallest pore diameter of 4.5 nm is observed from the PtPd sample with volume ratio of 1:1.1 The other three samples (1:3, monometallic Pt, and monometallic Pd) have pore sizes of 4.9 nm, 5.0 nm and 5.2 nm, respectively. The synthesized samples shows similar pore size with the work done by Gosh et al., about 5 nm [23]. From Fig. 1(a - c), the porosity becomes more prominent

compared to the monometallic samples. This shows that monometallic Pd and Pt produces denser structures and less porosity.

The proposed chemical reaction is given by Eq. 1.

$$H_2PtCl_6 + H_2PdCl_4 \xrightarrow{NaBH_4} PtPd + 2H_2 + 5Cl_2$$
(1)



Fig. 1. FESEM images of the PtPd samples prepared with volume ratio (a) 1:1, (b) 1:3, (c) 3:1, (d) monometallic Pd and (e) monometallic Pt at magnification of 100kx (scale: 500 nm).

From the above reaction (Eq. 1), H₂PtCl₆, and H₂PdCl₄ are the metal precursors reduced by adding NaBH₄. Because the reduction process follows the electronegativity table, the Pt (II) precursor was reduced first, yielding Pt (0) nanoparticle. This was followed by a Pd (II) precursor, which resulted in Pd (0) resulting in the black product of PtPd. The formation of a non-ordered porous structure mainly depends on the reduction rates. It has been established that the reducing power of reductant, the type of solvent, and counter-ion metal salt affect the formation of nuclei [23]. The metal ion reduced by NaBH₄ could occur instantaneously since a strong reducing agent was used. The large numbers of nuclei form the nanoparticles, which are the primary units of the network, followed by spontaneous destabilization. Subsequently, fusion and growth of metal nanoparticles led to a three-dimensional interconnected backbone. The dielectric constant and high ionic strength of solvent also helps the colloidal particles to overcome the repulsion barrier and undergo coalescence with one another. During this process, NaBH₄ gets hydrolyzed, resulting in the formation of hydrogen gas bubbles which act as dynamic templates to generate pores within the agglomerates leading to the formation of hollow structures [23].

Fig.2 demonstrates the XRD patterns of the PtPd nanosponges prepared at different volume ratios. The prominent diffraction peaks correspond the reflection planes of (111), (200), (220), (311), and (222), which confirmed the existence of polycrystalline PtPd face-centred cubic phase. The peaks are in good agreement with the reference database of Pt (JCPDS no: 01-087-

0640) and Pd (JCPDS no: 01-087-0645). The crystallinity of PtPd nanosponges prepared at different volume ratios increased in this order 1:1 < 1:3 < 3:1. The average crystallite size of the bimetallic nanoparticles was calculated from the (111) plane using the Debye-Scherer equation (Eq. 2) [27].

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{2}$$

where λ , β , θ are the wavelength of X-ray radiation used (Cuk α = 0.15406 nm), the full-width-athalf maximum (FWHM) of diffraction peak and the Bragg diffraction angle, respectively. The average crystallite size is 1.65, 2.00 and 2.53 nm for PtPd (1:1), PtPd (1:3) and PtPd (3:1) samples, respectively. The observed increase in crystallite size could be attributed to an increase in the crystalline due to a decrease in the peak width at half maximum.



Fig. 2. XRD patterns of the PtPd nanosponges synthesised at different volume ratio of (a) Pt: Pd (1:1), (b) Pt: Pd (1:3) and (c) Pt: Pd (3:1).

Next, the dislocation density (δ) otherwise defined as the length of dislocation lines per unit volume is estimated as follows [28]:

$$\delta = \frac{1}{D^2} \tag{3}$$

The strain (ϵ) of the PtPd is then determined as follow [28]:

$$\varepsilon = \frac{\beta cos\theta}{4} \tag{4}$$

The interplanar distance (d) is obtained for all sets by using Bragg's formula as follows:

$$d = \frac{h\lambda}{2\sin\theta} \tag{5}$$

where h is a constant equal to 1. The lattice constants (a) and (c) are subsequently deduced using the following works as reference [28]:

$$a = \frac{\lambda}{\sqrt{3}\,\sin\theta} \tag{6}$$

$$c = \frac{\lambda}{\sin\theta} \tag{7}$$

The above parameters are given in Table 1 in detail.

Lattice Sample Dislocation Interplanar Strain, ε Lattice PtPd Density, δ Distance, d constant, a constant, c 1:1 0.367 0.020 0.08 0.10 0.17 1:3 0.250 0.017 0.08 0.10 0.17 0.013 0.08 0.17 3:1 0.156 0.10

Table 1. Structural properties of PtPd nanosponges growth at different volume ratio.

From Table 1, it became apparent that the amount of metal composition and nature of alloy were an important variable. Since dislocations are nucleated by the movement of the existing dislocations, it seems reasonable to expect that PtPd (1:1) sample exhibit the highest dislocation density because of small crystallite size. The strain also increases corresponds to the multiplication of dislocation during the deformation of the crystal. Crystals of lower alloying composition tend to be soft, often bend upon cleaving, thereby produced higher dislocation density. In contrast, crystal having high alloying composition are hard, difficult to cleave, thus show decrease in dislocation density. Additionally, the dislocation density is decreased by a process of annihilation which has been documented by metallurgist [29]. Dislocation density can affect the electrocatalytic activity of a material in several ways. Dislocations can create local strain fields that promote the adsorption and activation of reactants, leading to increased electrocatalytic activity.

Fig. 3 shows the CV curves for the prepared samples carried out in KOH aqueous solution. All samples exhibited a strong peak related to desorption (or adsorption) of adsorbed hydrogen below -0.5 V, except for the PtPd (1:3) samples, where it barely sees any significant peak in the CV curve. In the positive scan, metal alloys are mainly oxidized between -0.4 V and -0.3 V which is the surface oxidation onset for PtPd 1:3 and 3:1, for 1:1 the oxidation seems to start at a more positive potential. In the negative scan, the oxidized metals alloys are between -0.1 V and -0.65 V. This is the surface oxidation onset for PtPd 1:3 and 3:1, for 1:1 the oxidation seems to start at a more positive potential. Based on the CV curves in Fig. 3, the electrochemical surface area (ECSA) can be obtained using Eq. 8.

$$ECSA = \frac{Q_H}{0.21L} \tag{8}$$

The Q_H (mC/cm²) is the integration area of the desorption (or adsorption) of adsorbed hydrogen obtained from a CV curve between – 0.8 V and – 0.5 V, and *L* corresponds to the quantity of solution dropped on glassy carbon (g/cm²), and 0.21 mC/cm² is the charge required to reduce a monolayer of hydrogen adsorption [30]. The results are tabulated in Table 2. The highest value of the ECSA is found to be 14.25 m²/g, which is obtained from the PtPd 1:1 sample. The lowest ECSA value is 0.05 m²/g which is from the PtPd 1:3. The ECSA values for PtPd 3:1, monometallic Pt and monometallic Pd are 0.33 m²/g, 13.53 m²/g and 9.65 m²/g respectively.

Sample	$Q_{\rm H} ({\rm mC/cm^2})$	ECSA (m^2/g)
Pt	0.284	13.53
Pd	0.203	9.65
PtPd 1:1	0.299	14.25
PtPd 1:3	0.001	0.05
PtPd 3:1	0.007	0.33

 Table 2. ECSA value for the synthesized PtPd nanosponges at different volume ratios and its single element.



Fig. 3. CV curves for for reaction with KOH at scan rate 50 mVs⁻¹.

The high ECSA value obtained for the PtPd (1:1) sample could be attributed to the smaller particle, uniform particle dispersion and high dislocation density that can create local strain fields that promote the adsorption and activation of reactants, leading to increased electrocatalytic activity. Dislocations can affect the transport of electrons and ions in the material. Dislocations can act as barriers or facilitators to electron and ion transport, depending on their orientation and density. Therefore, the high density of dislocations of PtPd (1:1) can increase the number of pathways for electron and ion transport, leading to improvements of its electrocatalytic activity. Next, the performance of the synthesised PtPd towards methanol oxidation was studied by adding 10 mL of 1.0 M methanol (MetOH) in the KOH solution (Fig.4). The inset figure shows the CV profiles of Pt and Pd catalyst for comparison. During the CV scan, each catalyst showed two unique oxidation peaks. The methanol oxidation is related to the peak obtained in the forward scan. Among the alloyed samples, only PtPd (1:1) exhibit the typical behavior of methanol single mechanism at a clean polycrystalline PtPd surface with the appearance of an oxidation peaks at -0.1 V in the forward scan (J_f) and a reduction peak at -0.2 V in the reverse going potential scan (J_b) . The single peak observed in the forward scan ascribed to direct pathway, in which methanol is directly dehydrogenated to form CO₂. The reverse scan oxidation peak aids in regenerating active sites on the catalyst surface for subsequent oxidation reactions. As the potential was reduced to below -0.4 V, the current decreased due to slower diffusion rate upon cathodic deposition of adsorbed hydrogen into the PtPd lattice [30].

Table 3 presents the value of J_b and J_f for each sample and the ratio of J_b/J_f . According to literature, the J_b/J_f value of 1 indicates high methanol oxidation activity. The J_b/J_f value for the PtPd (1:1) was found to be 0.34, which is the closest value to 1 when compared to other samples. This agrees with the highest ECSA value observed for this sample. This indicates the better carbon poisoning management capacity of the sample due to its higher resistance towards carbon monoxide adsorption. Although both PtPd 3:1 and 1:3 exhibits reasonable ECSA values, the J_f and J_b values were found to be small. This implies that the PtPd synthesised with these compositions

are catalytically active toward KOH solution, but inactive during the electrooxidation of methanol, probably due to the high adsorption of carbon monoxide on the surface-active sites.



Fig. 4. CV curves for all samples PtPd bimetallic alloy nanosponges for reaction with KOH plus methanol at scan rate 50 mVs⁻¹.

Table 3. The J_b and J_f value of PtPd electrocatalyst at different metal composition.

Sample	$J_b(mA/cm^2)$	$J_{f} (mA/cm^{2})$	J_b/J_f
Pt	0.80	3.41	0.20
Pd	0.44	2.96	0.15
PtPd 1:1	0.37	1.1	0.34
PtPd 1:3	-	-	-
PtPd 3:1	-	-	-

A chronoamperometry (CA) test was also caried out to evaluate the electrocatalyst stability of the synthesised PtPd samples. The current-time responses were monitored for 200 s cycle at the bias of -0.25 V in an aqueous solution of 1 M KOH + 1 M methanol. The results obtained are shown in Fig. 5. As expected, the CA curve of the PtPd 1:1 show the highest stability at 200 s. This probably due to its higher ECSA value of 14.25 m^2/g compared to the other sample. The current dissipation is mainly due to the accumulation of CO on the PtPd surface immediately after the voltage step is applied. The CA curves of the Pt sample ranked second in terms of stability, being the sample with the second high ECSA value of 13.53 m^2/g in ECSA value. The Pd, PtPd 1:3 and PtPd 3:1 exhibit low current stability due to their lower ECSA values. This suggests that the samples possessed fewer catalytic sites leading to more irregular MOR activity in the alkaline medium.



Fig. 5. Chronoamperometric curves for all synthesized PtPd nanosponges scanning for 200 s at bias voltage of -0.25 V.

Based on the results, PtPd 1:1 ratio was further studied on the effect of capping agent on the properties of PtPd. FESEM images (Fig. 6a and 6c) show that PtPd synthesized with PEG, and PVP exhibit a non-ordered porous structure distributed on the surface. Both samples form an open interconnected network backbone with smaller hollow structures were observed for samples assisted with PVP. As for PtPd synthesized with PEG, the sample consists of agglomerated cubic particles with several small pores (inset Fig. 6a). The explanation on the formation of a nonordered porous structure (Fig. 6a and 6c) has been discussed earlier. The use of PVA as a capping agent produced a microporous architecture that has an interconnected 3-D porous network with randomly oriented structures. PVA was used as a cross-linking agent, which helped build the porous network structure by interconnecting the PtPd while maintaining its integrity during the synthesis [31]. Introducing PVP in the synthesis produced a finer ligament-pore structure than the capping agent's absence. This is possibly due to the restrictions on free diffusion of Pt and Pd adatoms due to the adsorption of PVP macromolecules [32]. Similar behavior was observed for PEG, but the particles tend to agglomerate and decrease the porous cavity. Given the above results, the next question is whether the interactions among these samples can have a profound impact on their MOR activities in alkaline electrolytes. Fig. 7a shows the representative CV curve of PtPd synthesized with and without a capping agent (inset). Two peaks can be observed between -0.8 V-0.5V for PtPd assisted PVP, PEG and without capping agent, attributed to the hydrogen adsorption/desorption peak. During the forward scan, the oxidation of Pt/Pd happens at a higher potential, which can be seen around -0.1 to 0.4V vs Ag/AgCl, and hence potentially generate surface oxides.



Fig. 6 FESEM image of PtPd nanostructure assisted with a) PEG, b) PVA, and c) PVP, respectively.

During the reverse scan, the produced oxide is reduced in the potential range of 0 to -0.4 V versus Ag/AgCl, the typical maxima for Pt and Pd-based materials. A noticeable difference in the cyclic voltammetry curves for the PtPd synthesized with the capping agent is observed from the negative shifts of the oxide formation/ reduction peaks compared to PtPd without the capping agent. The high charge corresponding to the hydrogen refers to the hydrogen adsorption/desorption and the oxide reduction peak on PtPd synthesized with PVP is indicative of high ECSA compared to samples prepared with PEG, PVA, and without the capping agent. Table 4 demonstrates the value of ECSA of PtPd alloyed catalyst with and without capping agent. Among the capping agent, PtPd synthesized with PVP demonstrates the highest ECSA of 692.7 m^2/g compared to the sample without a capping agent (287.8 m^2/g). The high ECSA is probably due to the high surface area of the sample. The low ECSA values of PtPd synthesized with PVA and PEG suggest that these two capping agents are prone to block the active surface sites and reduce the catalyst's efficiency to perform a redox reaction at the surface.



Fig. 7. CV curves of the PtPd prepared using different stabilizing agents in a)1 M KOH, b) 1 M KOH + 1 *M MetOH. The inset figure shows the curve of PtPd synthesized without a capping agent.*

Fig. 7b demonstrates the CV profiles of the synthesized PtPd in the presence of a capping agent toward methanol oxidation. The inset figure shows the CV profiles of PtPd without a capping agent for comparison. The methanol oxidation was characterized by two current peaks on the forward and backward scan. In the forward scan, the peak observed is related to the oxidation of freshly chemisorbed species from methanol adsorption. While the backward scan peak representing the elimination of carbon element formed during the oxidation of chemisorbed species. From Fig. 7b, it can be observed that the current density of PtPd synthesized with PVA, PVP, and without capping agent increases rapidly in the forward (anodic) direction. The magnitude of the reverse oxidation peak current density is less than the anodic peak current density which suggests the trend toward complete oxidation of methanol. Only PtPd synthesized with PVA shows further reactions on the surface covered by reversible OH_{ads} species, implying a faster kinetics reaction [11]. The current maxima is observed at 0.4 V, associated to the balanced between the rate of methanol dehydrogenation and dehydrogenated products with OH_{ads} species [33]. The current is rapidly decrease once reach the maximum reaction rate, due to the fast transition from the reversible to the irreversible state of oxygenated species [33]. Whereas PtPd synthesized with PEG does not exhibit distinct oxidation peaks during the CV scan. The suppression of the oxide reduction peak during the reverse scan implies the presence of unoxidized organic residue during the MOR process which also suggesting that there is formation of surface oxides which block the oxidation reaction to occur. This suggests that PEG probably blocks the active sites and hinders any catalytic reaction at the surface. PtPd synthesized with PVP is a promising catalyst for MOR reaction due to its high ECSA value and high anodic current density compared to other capping agents and PtPd synthesized without capping agents. This is probably due to small size particles that contribute to the large surface area for catalytic reaction to occur.

Samples PtPd	$Q_{\rm H} [{\rm mC/cm^2})$	ECSA [m ² /g]
W/O capping agent	0.12	287.8
PVA	0.05	121.9
PEG	0.07	175.6
PVP	0.28	692.7

Table 4. Electrochemical Surface Area (ECSA) of PtPd synthesized with and without a capping agent.

4. Conclusions

In summary, the PtPd bimetallic alloy nanosponges were synthesized by the chemical reduction method at different volume ratio and different types of capping agents. The difference in volume ratio and capping agents was found to influence the structural and the catalytic behaviour of the catalyst. The, PtPd (1:1) sample exhibited the highest catalytic activity for methanol oxidation reaction as it has a higher current density in anodic reaction and larger ECSA value of 14.25 m²/g. Among the samples, PtPd synthesized with PVP is a more promising catalyst for methanol oxidation reaction as it has a higher current density in anodic reaction, larger ECSA, and better crystallinity than PVA, PEG, and PtPd without a capping agent.

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References

[1] M.H. de Sá, A.M.F.R. Pinto, V.B. Oliveira, Energies 15(10), 3787 (2022); https://doi.org/10.3390/en15103787

[2] F. Samimi, M.R. Rahimpour, "Direct Methanol Fuel Cell", Elsevier, Amsterdam, 381 (2018); https://doi.org/10.1016/B978-0-444-63903-5.00014-5

[3] M.F. Sgroi, F. Zedde, O. Barbera, A. Stassi, D. Sebastián, F. Lufrano, V. Baglio, A.S. Aricò, J.L. Bonde, M. Schuster, Energies 9(12), 1008 (2016); <u>https://doi.org/10.3390/en9121008</u>

[4] H.A. Gasteiger, S.S. Kocha, B. Sompalli, F.T. Wagner, Applied Catalysis B: Environmental 56(1-2), 9 (2005); <u>https://doi.org/10.1016/j.apcatb.2004.06.021</u>

[5] J. Zeng, C. Francia, C. Gerbaldi, V. Baglio, S. Specchia, A.S. Aricò, P. Spinelli, Journal of Solid State Electrochemistry 16, 3087 (2012); <u>https://doi.org/10.1007/s10008-012-1750-3</u>

[6] L. Mazzapioda, C.L. Vecchio, A.S. Aricò, M.A. Navarra, V. Baglio, Catalysts 9(12), 1017 (2019); <u>https://doi.org/10.3390/catal9121017</u>

[7] X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, Z.S. Liu, H. Wang, J. Shen, Journal of Power Sources 165,739 (2007); <u>https://doi.org/10.1016/j.jpowsour.2006.12.012</u>

 [8] E. Christoffersen, P. Liu, A. Ruban, H.L. Skriver, J.K. Nørskov, Journal of Catalysis 199(1), 123 (2001); <u>https://doi.org/10.1006/jcat.2000.3136</u>

[9] M. K. Min, J. Cho, K. Cho, H. Kim, Electrochimica Acta 45(25-26), 4211 (2000); https://doi.org/10.1016/S0013-4686(00)00553-3 1260

- [10] T. Toda, H. Igarashi, H. Uchida, M. Watanabe, Journal of Electrochemical Society 146(10), 3750 (1999); <u>https://doi.org/10.1149/1.1392544</u>
- [11] S.S. Mahapatra, J. Datta, International Journal of Electrochemistry 2011(563495), 1 (2011); https://doi.org/10.4061/2011/563495

[12] K. Dong, H. Dai, H. Pu, T. Zhang, Y. Wang, Y. Deng, International Journal of Hydrogen Energy (2023); <u>https://doi.org/10.1016/j.ijhydene.2023.05.283</u>

[13] L. Shen, J. Ying, G. Tian, M. Jia, X.Y. Yang, Chemistry An Asian Journal 16(9), 1130 (2021); <u>https://doi.org/10.1002/asia.202100156</u>

[14] J. Wu, L. Qi, H. You, A. Gross, J. Li, H. Yang, Journal of The American Chemical Society 134, 29, 11880 (2012); <u>https://doi.org/10.1021/ja303950v</u>

[15] X. Huang, Y. Li, Y. Li, H. Zhou, X. Duan, Y. Huang, Nano Letter 12(8), 4265 (2012); https://doi.org/10.1021/nl301931m

[16] L. Sun, H. Wang, K. Eid, S.M. Alshehri, V. Malgras, Y. Yamauchi, L. Wang, Electrochimica Acta 188, 845 (2016); <u>https://doi.org/10.1016/j.electacta.2015.12.068</u>

[17] A.M. Landry, E. Iglesia, Journal of Catalysis 344, 389 (2016); https://doi.org/10.1016/j.jcat.2016.10.007

[18] D. Nelli, C. Roncaglia, S. Ahearn, M.D. Vece, R. Ferrando, C. Minnai, Catalysts 11(16), 718 (2021); <u>https://doi.org/10.3390/catal11060718</u>

[19] L.N. Zhou, X.T. Zhang, Z.H. Wang, S. Guo, Y.J. Li, Chemical Communications 52, 12737 (2016); https://doi.org/10.1039/C6CC07338G

[20] Z.C. Zhang, J.F. Hui, Z.G. Guo, Q.Y. Yu, B. Xu, X. Zhang, Z.C. Liu, C.M. Xu, J.S. Gao, X. Wang, Nanoscale. 4, 2633 (2012); <u>https://doi.org/10.1039/c2nr12135b</u>

[21] B. Lim, M. Jiang, T. Yu, P.H.C. Camargo, Y. Xia, Nano Research 3, 69 (2010); https://doi.org/10.1007/s12274-010-1010-8

[22] H. Wang, S. Liu, H. Zhang, S. Yin, Y. Xu, X. Li, Z. Wang, L. Wang, Nanoscale 12(25), 13507 (2020); <u>https://doi.org/10.1039/D0NR02884C</u>

[23] S. Ghosh, B.R. Jagirdar, Chemistry Select 3(25), 7184 (2018); https://doi.org/10.1002/slct.201801562

[24] Y.X. Gan, Y. Zhang, J.B. Gan, AIMS Material Science 5(6), 1141 (2018); https://doi.org/10.3934/matersci.2018.6.1141

[25] J. Wu, S. Shan, H. Cronk, F. Chang, H. Kareem, Y. Zhao, J. Luo, V. Petkov, C.J. Zhong, Journal of Physcal Chemistry C 121(26), 14128 (2017);

https://doi.org/10.1021/acs.jpcc.7b03043

[26] T. Guo, H. Xiang, W. Li, H. Li, H. Chen, S. Liu, G. Yu, ACS Sustainable Chemistry & Engineering 8(7), 2901 (2020); <u>https://doi.org/10.1021/acssuschemeng.9b07189</u>

[27] G. S. Kumar, N. R. Reddy, B. Sravani, L.S. Sarma, T.V. Reddy, V. Madhavi, S.A. Reddy, Journal of Cluster Science 32, 27 (2021); <u>https://doi.org/10.1007/s10876-019-01752-z</u>

[28] A. S. Z. Lahewil, Y. Al-Douri, U. Hashim, N. M. Ahmed, Procedia Engineering 53, 217 (2013); <u>https://doi.org/10.1016/j.proeng.2013.02.029</u>

[29] J.W. Hall, H.F. Rase, Industrial & Engineering Chemistry Fundamentals 3(2), 158 (1964); https://doi.org/10.1021/i160010a013

[30] N. Elgrishi, K.J. Rountree, B.D. McCarthy, E.S. Rountree, T.T. Eisenhart, J.L. Dempsey, Journal of Chemical Education 95(2), 197 (2018); https://doi.org/10.1021/acs.jchemed.7b00361

[31] H. Wang, W. Wang, Y. Zhao, Z. Xu, L. Chen, L. Zhao, X. Tian, W. Sun, RSC Advances 8(15), 7899 (2018); <u>https://doi.org/10.1039/C8RA00113H</u>

[32] Z. Jiadong, S. Yanyan, Z. Sun, Nanotechnology 29(48), 485401 (2018); https://doi.org/10.1088/1361-6528/aae05e

[33] E. H Yu, K. Scott, R.W Reeve, Journal of Electroanalytical Chemistry 547(1), 17 (2003); https://doi.org/10.1016/S0022-0728(03)00172-4