**Research Article**

# The Effect of Heat Treatment on Nanoparticle Size and ORR Activity for Carbon-supported Pd–Fe Alloy Electrocatalysts

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**Abstract**

The synthesized carbon-supported Pd-Fe alloy electrocatalysts were characterized for the purpose of the fuel cell cathode oxygen reduction reaction (ORR). The synthesized catalysts were characterized in terms of structural morphology and catalytic activity by XRD and electrochemical measurements. Surface cyclic voltammetry was used to confirm the formation of the Pd–Fe alloy. The catalysts were heat-treated at temperatures ranging from 300 °C to 700 °C for different ageing times, in order to improve activity and stability. The average particle size of 10.16 nm, and the highest ORR catalytic activity were obtained at the optimal heat-treatment temperature 300 °C for 3h. Electrocatalytic ORR activity was also examined in an acidic solution containing methanol. The results showed that the synthesized Pd–Fe/C catalyst has methanol tolerant capabilities.

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# 1. Introduction

The high cost arising from the use of expensive noble metal catalysts in the current PEMFC technique is one of the main problems. Electrocatalysts based on Platinum are exclusively used for catalyzing oxygen reduction reaction (ORR) and methanol oxidation reaction (MOR) in Direct Methanol Fuel Cells (DMFCs) [1-4]. The widespread commercialization of DMFCs hindering by several limitations such as the high cost, the low availability of platinum and the irreversible inactivation of the catalysts by CO-like poisoning species [5, 6]. It is therefore desirable to develop low cost catalysts with comparable activity towards methanol oxidation reaction and better CO-tolerance for DMFCs. The important and urgent task for fuel cell investigators is the research on non-Pt catalyst. Unfortunately, in principle, only noble metals can be stable in the acidic environment of PEMFC which limited the choice of catalysts for PEMFC. Pd could be a good candidate, among alternative noble metals, not only because Pd is one of the Pt-group metals and has been applied in many heterogeneous catalysis processes, but it is also less expensive and relatively abundant in comparison with Pt. However, Pd was found to be inferior to Pt towards most fuel cell relevant reactions, except for the electro oxidation of formic acid [7]. In recent years, much effort has been devoted to the development of Pd alloys as alternative catalysts for PEMFC, especially for the reduction of oxygen at the cathode [8-10]. Some of these alloys have exhibited activities comparable to that of Pt. Though encouraging results have been achieved, there is still a lack of systematic understanding for the rational design of Pd-based catalysts. We report herein a combined study of initio calculations and electrochemical experiments on tuning the surface reactivity of Pd via lattice straining which was realized by alloying Pd with Fe in the core of a nanoparticle and enriching Pd on the surface. Usually, in order to promote alloy formation the Pt-based [11, 12] and Pd-based [13] alloy catalysts are prepared and/or post-treated at high temperatures in inert or reducing atmospheres. However, a decrease in the surface area and catalytic activity as results of the thermal treatment at high temperatures leads to an undesired particle growth. Therefore, catalyst preparation methods that can offer high degrees of alloy homogeneity with small particle size and high surface area at moderate temperatures are needed. Theoretical calculations and experimental data demonstrated that, upon annealing at elevated temperatures, Pd-M alloys undergo phase segregation, in which the noble metal Pd migrates to the surface forming a pure Pd over-layer on the bulk alloys [14-18]. The electronic structures of the metal over-layers can alter significantly upon bonding with the substrate metal, and, in turn, their catalytic properties can change [19- 21]. Nørskov et al., correlated the electronic structure of the surface metal (represented as the energy centre of the valence d-band density of states) and its catalytic activity; there model has been applied to explain the catalytic activity and electrochemical behaviour of some strained surfaces and metal over-layers [22, 23]. Savadogo et al., [9] reported that, the catalytic activity of $Pd_3Fe/C$ electrocatalyst prepared by thermal treatment surpassed that of the state-of-the-art Pt/C catalyst and that the enhanced catalytic activity is due to the more favourable Pd–Pd interatomic distance. The particle size of Pd-based catalysts, as reported in literatures [24-29], is large, thus there proves to be significant room for improvement in ORR mass activity. Challenges to be met for the preparation of improved Pd alloy catalysts include the need for synthesis procedures resulting in catalysts with desirable composition, small particle size and a narrow size distribution. Abo Zeid et al., [30] investigated the effect of the heat-treatment temperature on catalytic activity of Pd-Co alloy in the range of temperature 300-700 °C and they concluded that the optimal heat-treatment temperature was 300 °C. The heat-treated catalyst at 300 °C exhibited an enhanced ORR activity due to the smaller average mean particle size of ca, 12 nm, compared to those treated at other temperatures. In a continuing effort to improve the catalytic activity of Pd–Fe alloys, this paper focuses on the combined effect of the ethylene glycol (EG) and sodium borohydride ($NaBH_4$)  as a synthetic reducing agents with the presence of

polycation (PDDA) on catalyst morphology and on the corresponding ORR catalytic activity. The effects of heat treatment during the a temperature range from 300 to 700 $^o$C on the catalyst morphology are characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HRTEM), energy dispersive spectroscopy (EDS), Cyclic Voltammetry, and electrochemical polarization measurements in rotating disk electrodes (RDE) and single-cell PEMFC for ORR.

# 2.  Experimental

## 2.1. Catalyst Synthesis

Carbon-supported $Pd_{70}$-$Fe_{30}$ catalysts with 20 wt% metal in carbon were synthesized by a modified polyol reduction process. Required amounts of $(NH_4)_2PdCl_4$ and $FeCl_2$-$6H_2O$ to obtain 100 mg of $Pd_{70}$-$Fe_{30}$/C (20 wt%) were dissolved in deionized water. 30 ml from ionic polycation (PDDA) was added to 30 mL ethylene glycol and sonicated for 15 min. 40 ml of ethylene glycol refluxed at 130 $^\circ$C under stirring, PDDA was added drop wise to the ethylene glycol under stirring in 10 times with the appropriate amounts of $Pd_{70}Fe_{30}$ to give an atomic ratio of PDDA: $Pd_{70}Fe_{30}$ = 7:1. The mixture was kept under stirring for 2h at 130 $^\circ$C. A fresh solution containing 200 mg of $NaBH_4$ in 40 ml of deionized water was added. The colour of the solution was observed to change from yellow to black, indicating the processing of the reduction reactions. The mixture was kept under stirring and refluxed at 130 $^\circ$C for 1h, cooled to room temperature, an appropriate amount of carbon (Vulcan XC 72R) was added, stirred overnight, and the slurry was filtered, washed with water and ethanol, and dried overnight in vacuum oven at 70 $^\circ$C. These, as prepared samples are denoted as $Pd_{70}Fe_{30}$/C -ASP. The synthesized samples were heated at 300, 500, and 700 $^\circ$C in a flowing mixture of 10% $H_2$-90% Ar for 3 hours, followed by cooling to room temperature in order to study the effect of heat-treatment temperature on the catalytic activity. In order to study the effect of ageing time    on the catalytic activity, the samples were aged for 1 h, 2 h, 3 h, 4 h and 5 h at 300 $^\circ$C in a flowing mixture of 10% $H_2$-90% Ar followed by cooling to room temperature.

## 2.2. Material Characterization

XRD measurements of $Pd_{70}Fe_{30}$/C catalysts were carried out on a Philips Pan analytical X-ray diffractometer in The Korea Basic Science Institute. The detailed description of the XRD measurements was indicated in [30]. In order to estimate the particle size from XRD, Scherrer's equation was used [31]. For this purpose, the (111) peak of the Pd face-centered-cubic (fcc)/fct structure around 2 $\theta$ = 40° was selected. Morphological and particle distribution studies were carried out with a JEOL 2010F high-resolution transmission electron microscope (HRTEM) operated at 200 keV [30].

## 2.3. Electrochemical Measurements

Cyclic Voltammetric (CV) characterizations were carried out with a standard single-compartment three-electrode cell having a Pt mesh counter electrode, a glassy carbon (5 mm dia.) working electrode and a leak-free (Ag/AgCl, 3.5 M KCl) with a double-junction chamber (Cypress) reference electrode, employing a biologic VSP potentiostat (France) [30]. The CV plots were conducted in $N_2$ purged 0.1 M $HClO_4$ at a scan rate of 50 mV/s between -0.2 and 0.8 V (vs. Ag/AgCl) at ambient conditions. Before recording the voltammograms, the catalyst surface was cleaned by cycling 50 times between -0.2 and 0.8

V (vs. Ag/AgCl). Rotating disk electrode (RDE) experiments were conducted with a glassy carbon disk electrode (5 mm dia.) mounted onto an interchangeable RDE holder (Pine Instruments, France) in $O_2$ saturated 0.1 M $HClO_4$.

# 3. Results and Discussion

## 3.1. Physical Characterization of Pd-Fe/C Bimetallic Catalysts

The XRD patterns of the carbon-supported Pd–Fe, (a) aged at different temperatures for 3h and (b) aged at 300 °C for different ageing times are shown in Fig. 1.   Five main characteristic peaks of the fcc crystalline Pd (JCPDS Card 00-005-0681) [32], namely the planes (111), (200), (220), (311), and (222) was observed in Fig. 1 (a). The five diffraction peaks in the Pd–Fe (70:30 atom %) alloy catalysts are shifted to higher 2θ values compared to those of Pd–Fe upon heat-treatment, suggesting incorporation of Fe into the Pd lattice. A shift of diffraction peaks to higher angles with increasing aging temperature indicating the contraction of the lattice and an increase in the degree of alloying of Fe with Pd. The reflections correspond to only a single fcc phase suggestive of the formation of a binary Pd–Fe alloy phase. The alloy constituents were thoroughly mixed in the crystal system which indicated by the absence of peaks for Fe or its oxides. The diffraction peak at around 2θ =25° corresponds to the (0 0 2) plane diffraction of the hexagonal structure of the carbon Vulcan.
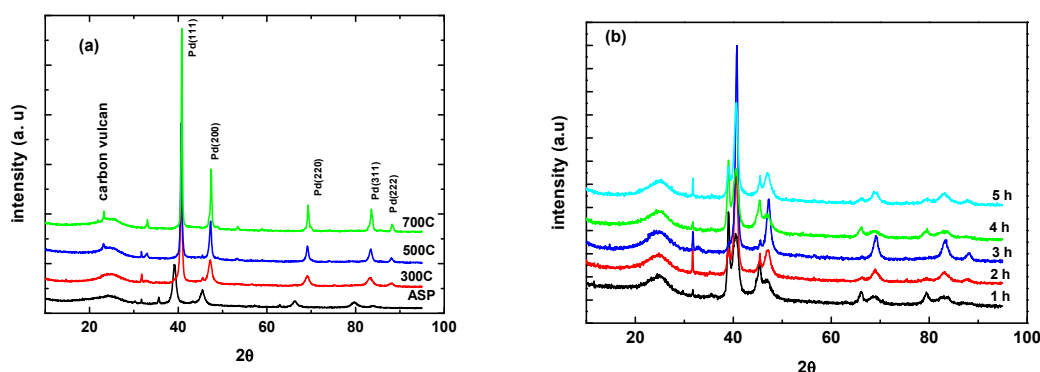


**Fig. 1** XRD patterns of the carbon-supported Pd–Fe heated, (a) at different ageing temperatures for 3h, (b) at 300 °C for different ageing times.

In Fig. 1b, there are also five main diffraction peaks for fccPdFe/C catalysts aged at 300 °C during different times. With increasing the ageing time, these diffraction peaks shift to a higher angle. Such angle shifts reveal alloy formation between Pd and Fe with increase in ageing times during the aging temperature, and indicate lattice contractions, which are caused by the incorporation of Fe into the Pdfcc structure. However; reflections corresponding to only a single fcc phase are found on aging at 700 °C, indicating the formation of a binary Pd–Fe alloy phase at higher temperatures.

From Fig. 1(a) it was observed that, the optimal temperature should be thus around 300 °C for studied catalysts. Higher temperatures, such as 500 °C and 700 °C, resulted in an increase in particle size and a decrease in active surface area (Fig.2). The mean particle sizes calculated from XRD patterns (PSXRD)

for the catalyst alloy are shown in Table 1.

**Table 1** Characteristics of prepared Pd–Fe/C (Pd:Fe = 70:30 atom%) alloy catalyst by XRD .

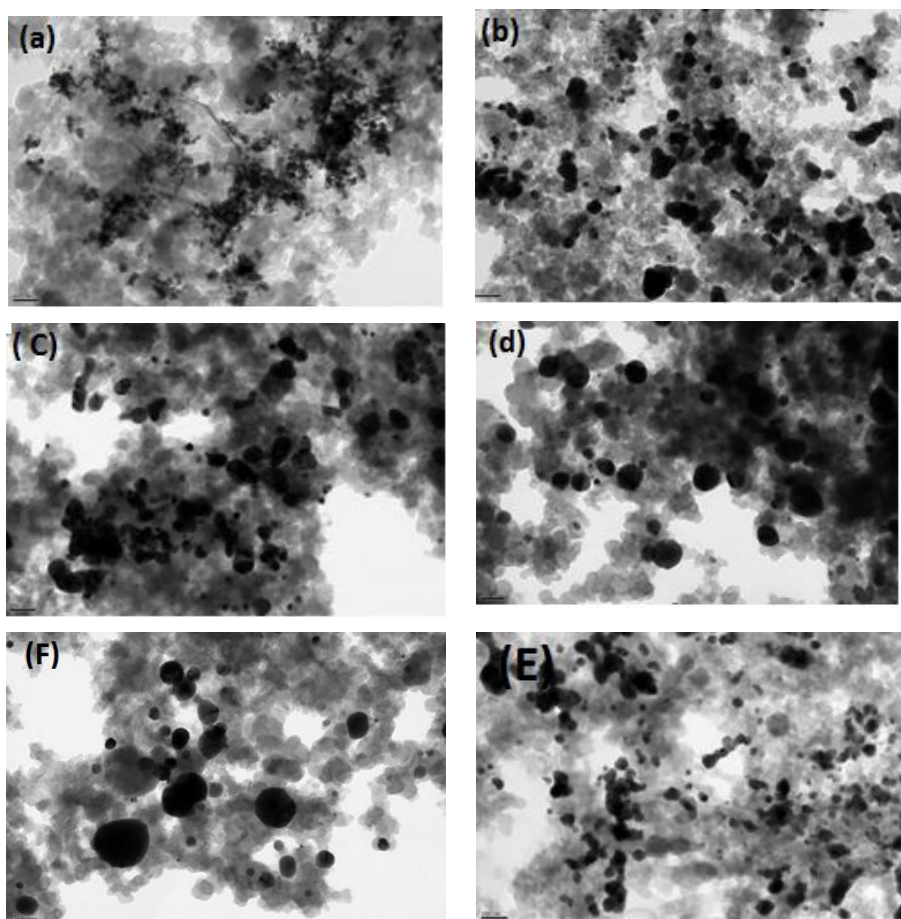| Heat treatment property | | Ageing temperatures | | | Ageing times at 300 ºC | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | ASP | 300 ºC for 3h | 500 ºC for 3h | 700 ºC for 3h | 1h | 2h | 3h | 4h | 5h |
| PSXRD (nm) | 10.64 | 16.15 | 25.3 | 34.07 | 12.07 | 14.87 | 16.15 | 16.89 | 19.71 |
| SXRD | 50.21 | 33.08 | 21.11 | 15.68 | 44.26 | 35.93 | 33.08 | 31.63 | 27.10 |



**Fig. 2** TEM micrographs of the carbon-supported Pd–Fe (Pd:Fe = 70:30 atom%) (a) ASP sample and followed by aging for 3 h (b) at 300 ℃; (c) at 500 ℃ and (d) at 700 ℃, in (E) and (F) the studied sample aged at 300 ℃ for 1h and 5h respectively, all of these images with 100 nm magnification.

It's observed that, the mean particle size increases with increase the aging temperature and time for the

as-prepared catalysts. The particle surface area S in $m^2\ g^{-1}$ was calculated using the equation $S = 6000/d\ \rho$ for spherical particles [33], where d is the crystallite size (diameter) in nm obtained from the(111) diffraction line, XRD data (Fig. 1) using the Scherrer equation $d\left(A^{\circ}\right)=\kappa\lambda\ /\ \beta Cos\theta$, [31], and $\rho$ is the density of the Pd-Fe alloy (~11.23 g $cm^{-3}$). The XRD-determined surface areas (SXRD) are also provided in table 1. As indicated, SXRD decreases as the aging temperature for the as-prepared catalysts is increased. This decrease in the SXRD attributed to the agglomeration of the particles which results in the increase of particle size Fig. 2. From the results of the mean particle size and active surface area in the table 1 we can conclude that the optimal ageing time ranges from 3h to 4h at the optimal ageing temperature 300$^{\circ}$C.

As a comparison, a uniform distribution of catalyst particles with a predominant and regular spherical shape can be observed in all samples after aging at various temperatures. An increase in particle size with increasing aging temperature (Fig. 2b–d) may suggest agglomeration during heat treatment. These images indicate that, all the catalysts have a good dispersion on the carbon surface with a narrow particle size distribution. It is also observed that the average particle size is slightly higher than the untreated one (Fig.2a) and the heat-treatment appears to favour agglomeration as reported earlier [12, 31]. Particles with a few large sized ($\leq$ 35 nm) are also observed, which are formed as a result of the particles aggregation at higher temperatures. This observation was consistent with those calculated from XRD data. The obtained mean particle size is smaller than those reported by others for Pd-based catalysts, which may be beneficial for increasing in the ORR mass activity. Hence, the procedure for the catalyst preparation via a modified polyol reduction route may be a method for obtaining nano sized alloy catalysts with a good dispersion and a narrow particle distribution on a support. The aging for a long time increases the agglomeration process which results in an increase in particle size (Fig. 2 E, F).

## 3.2. Surface Cyclic Voltammograms of Pd–Fe/C Alloy Catalysts

CVs of the Pd–Fe/C synthesized catalysts are shown in (Fig. 3-a, b). These CVs were recorded in a 0.1M $HClO_4$ solution under $N_2$ atmosphere at 27 $^{\circ}$C after ageing the samples for 3h in the lower temperature range from 300 $^{\circ}$C to 700 $^{\circ}$C. The CV of Pd–Fe/C aged at 300 $^{\circ}$C for 3h (Fig. 3-a, b) shows large peaks in the potential range of -0.193 to –0.131V and -0.196 to-0.135 respectively, versus Ag/AgCl sat KCl 3.5 M, which correspond to the hydrogen adsorption/desorption processes. However, the other aged samples all exhibit smaller hydrogen peaks compared to those of the 300 $^{\circ}$C aged sample. It was observed that, the dissolution of hydrogen into bulk Pd–Fe/C might be restrained by the existence of the iron in the Pd lattice [29]. In the case of the aged sample (Pd–Fe/C) at 300 $^{\circ}$C, the degree of alloying for iron in Pd lattice to form the core shell is less than the other two aged samples (500 $^{\circ}$C and 700 $^{\circ}$C). Therefore, the larger peaks of the 300 $^{\circ}$C aged sample than the 500 $^{\circ}$C and 700 $^{\circ}$C samples may be ascribed to the lower degree of alloying for iron in this sample than the others. Normally, the areas under the hydrogen adsorption/desorption peaks in CVs can be used to estimate the electrochemically active surface areas (ESA) of a pure Pd catalyst. But in the case of alloy catalysts, such quantitative estimation may not be feasible. As a qualitative estimation, it can be seen that the Pd–Fe/C aged at 300 $^{\circ}$C sample shows the largest ESA compared to the other catalyst samples, which may be ascribed to the lower degree of aggregation and smaller particle size of this catalyst. Therefore, the aging at temperatures higher than 300 $^{\circ}$C for this kind of Pd-Fe/C alloys could negatively affect the morphology and electrocatalytic activity of the synthesized catalysts. In the case of an aged sample (Pd-Fe/C) at 300 $^{\circ}$C for 3 h, the degree of alloying for iron in Pd lattice to form the core shell is less than the other aged samples at higher ageing times (4 h

and 5 h). Therefore, the decrease of the peaks of the samples aged for 4 h and 5 h at 300 °C lower than that sample aged for 3 h may be attributed to the higher degree of alloying for iron in the samples aged for 4 h and 5 h. While ageing for long times might be changes both the degree of alloying and crystallite size which influence the activity. Therefore, ageing times longer than 4 h for this kind of Pd-Fe/C alloy catalyst, could negatively affect the morphology and electrocatalytic activity.
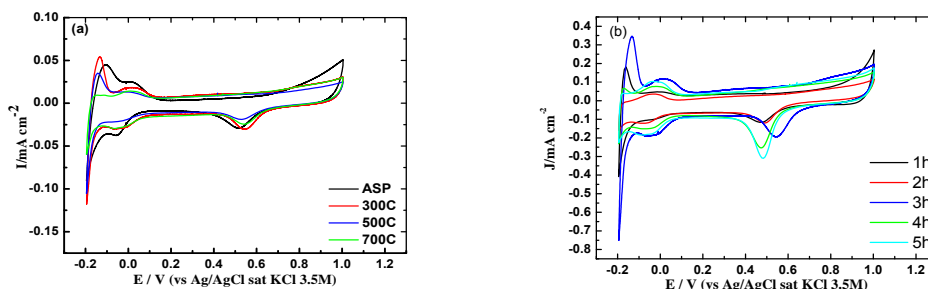


**Fig. 3** Cyclic voltammograms of Pd–Fe/C catalysts (a) aged at different temperatures ASP (as prepared sample), 300 °C, 500 °C and 700 °C and (b) aged at 300 °C for different ageing times 1h, 2h, 3h, 4h and 5h.

This result agrees with that reported by L. Zhang et al., [32] that, the optimal ageing temperature was found to be as low as 300 °C. There are no iron peaks apparent in the voltammetry, which might indicate that iron was fully incorporated into palladium to form an alloy, and a Pd-rich skin was formed on the alloy's surface. Such formation is supported by the XRD pattern revealing an asymmetrical diffraction line of the PdFealloy, Fig. 1.

## 3.2. Catalyst Activity Towards ORR as a Function of Ageing Temperatures and Time's.

Fig. 4a and b, shows the single scan voltammograms for the Pd–Fe/C alloys coated glassy carbon disc electrode at different ageing temperatures and times, in an oxygen-saturated 0.1M HClO$_4$ solution, and at ambient conditions. For comparison, an ORR curve for the as prepared Pd–Fe/C (Pd:Fe = 70:30 atom%) catalyst was also plotted in Fig. 4a and b. The ORR activity order was found from Fig. 4a, as follows: Pd–Fe/C (at 300 °C) > (at 700 °C) > (at 500 °C) > (without heat treatment ASP). The Pd–Fe/C alloy electrocatalyst, which was aged at 300 °C, shows the highest ORR activity. This behaviour ascribed to that, the catalyst which aged at higher temperatures has a larger particle size (smaller surface area) compared to those aged at lower temperatures. It`s observed that, the order of ORR performance is consistent with the particle size distribution order.
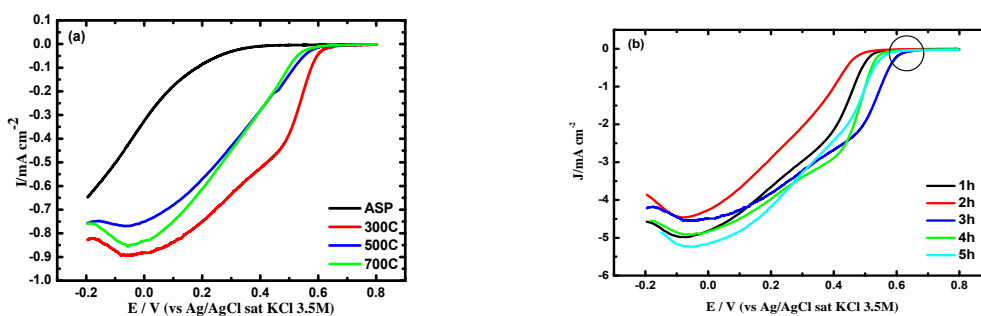


**Fig. 4** Single scan voltammograms for Pd–Fe/C catalyst (a) aged at different temperatures ASP (as prepared sample), 300 °C, 500 °C and 700 °C and (b) aged at 300 °C for different ageing times 1h, 2h, 3h, 4h and 5h.

Increasing the ageing temperature from 300 °C to 700 °C, causes an increase in particle size, leads to a decrease in ORR activity of the Pd–Fe/C alloy catalysts. After ageing at a high-temperature, the palladium atoms tend to migrate to the surface of the alloy nanoparticles because palladium and iron exhibit a strong trend toward segregation due to the large segregation energy difference between them [34, 35]. Thus, a Pd-rich "skin" should be formed on the Pd–Fe/C nanoparticles. Also, the ORR activity order is found from Fig. 4(b) as follows: Pd-Fe/C aged at (3 h) > 4 h>5 h >1 h>2 h. The electrocatalyst alloy which is aged at 300 ℃ for 3 h, showed the highest ORR activity.   This behaviour is attributed to that, the catalyst with high ageing time has a larger particle size (smaller surface area) compared to those aged for small periods at the same temperature. Increasing the ageing time from 3 h to 5 h caused an increase in particle size, thereby leading to a decrease in ORR activity of the PdFe/C alloy catalysts.

The data in Fig. 4 clearly demonstrates a decrease in catalytic activity for ORR with increasing ageing temperature due to a decreasing in surface area.

Additionally, differences in surface characteristics (e.g., crystallographic plane) and particle size distribution depending upon the synthesis method and heating temperature may influence the electrochemical activity. Thus, synthetic approaches that can give a high degree of alloying and homogeneity at lower temperature while keeping the particle size small with optimal surface characteristics have the possibility of improving the catalytic activity further.

## 4.  Conclusions

The effect of ageing temperature and time on the catalyst morphology and catalytic ORR activity are studied in more details for the Pd-Fe/C alloy.

It's found that, heat-treatments at appropriate temperatures 300 ℃, 500 ℃ and 700 ℃ for different ageing times improve the activity and stability of the catalysts. The optimal ageing temperature and time are found to be 300 ℃ for 3 h in the studied alloy. Before heat-treatment, a Pd–Fe/C alloy at room temperature showed a weak ORR activity. The Pd-Fe/C alloys contained unreduced Pd ions rather than Pd metal that were revealed by XRD and TEM measurements. It was found that, the increase in crystallite size and the degree of alloying significantly improves the catalyst durability. The kinetic study of ORR revealed that, this reaction catalysed by the Pd-Fe/C alloy electrocatalyst synthesized by this combined reducing agents.

## Acknowledgments

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