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Synthesize and thermal treatment of PdCr@carbon for efficient oxygen reduction reaction in proton-exchange membrane fuel cells

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Abstract:

A nanostructured PdCr@carbon catalyst is deposited on a supported carbon surface using the modified polyol reduction method for the oxygen reduction reaction (ORR) for the application in the proton exchange membrane fuel cell. The crystal structure and feature nanostructure of the PdCr@carbon were established using the XRD and TEM, while their catalytic activity was studied using the cyclic voltammetry and electrochemical polarization techniques. The estimated average crystallite size of PdCr is increased with the calcination temperature from 9.66 to 37.54 nm as the calcination temperature increased to 973 K, while the annealing time slightly affects the crystallite size. The TEM examination reveals the uniform distribution of the PdCr nanoparticles upon the carbon surface. The calcination temperature and time play an important factor in controlling the structural and morphology parameters of PdCr@carbon and the optimum activity and chemical stability were observed for samples calcined at 573 K for 3 h.

Keywords: PdCr@carbon; oxygen reduction; electrocatalyst; nanostructure; fuel cell

1. Introduction

The development of various properties of materials by the incorporation of the additional element(s) and/or heat treatment qualify the new products for various technological and industrial applications. Amongst; bimetallic is, a class of these materials, prepared by the substitution or doping of the transition metal with another noble metal and are showing a promising catalytic efficiency [1, 2]. Its generally known, modifying the electronic structure significantly affects the performance of the mixed-metal catalyst due to the improvement in the physical properties [3, 4].

Usually, Platinum (Pt), as well as Pt-based composites, are applied for the ORR, and their catalytic efficiency is significantly controlled by adjusting the nanostructure parameters such as the shape and size [5]. Unfortunately; the limited reserves, expensive of Pt, and deteriorative activity of Pt-based catalysts in practical operation preclude their commercial applications. Similarly, the metal-metal oxide can be applied as an efficient catalyst for the ORR [6, 7]. To overcome these difficulties the Pd-based binary alloys could be used as alternative metal. There are many studies about using the Pd-based materials nanocatalysts for the ORR [8-22]. To address this concern, the Pd nanoparticles with numerous morphologies such as icosahedron, sphere, spindle, cube, and rod are efficiently promoted for the Suzuki coupling reaction as well as the reduction of Cr(VI) [8]. Hussain *et al.* reviewed the recent progress in the developments of Pd nanostructured and other metal-based catalysts for organic transformation [9]. The nanostructured of Pd-25 at.% Cr shows greater active electrocatalysts for the ORR compared to Pd-33 at.% Cr catalyst [10]. In addition, Pd can be used as an efficient cathode in proton exchange membrane fuel cells [11, 12]. Besides the mentioned advantages of the Pd as a catalyst compared to Pt, it shows an increase in the catalytic activity [13, 14]. Moreover, the alloying of Pd with other metals such as Cr, V, Fe, Co, and Ni increased the catalytic activity [15-17]. Amongst these transition metals, the alloying of Ni and Cr leads to the formation of the stronger metallic bond with Pd and hence a greater enhancement in the catalytic activity [18, 19]. The Cr element is one of the most elements that show advantage when incorporated to Pd to form Pd-Cr alloy as it enhances the activity and stability of unary Pd [19]. Furthermore, the alloying of Cr and Pd improved the tolerance of Pd to poisoning due to the oxophilicity of Cr [20]. Besides Cr, other metals such as Mo, Ni, Co, and W can be incorporated to form Pd-based nanoalloys to be used as the electrocatalysts for replacing Pt-based ones toward the ORR and in fuel cells or other clean energy fields [5, 15, 22].

Studying the ORR in a proton-exchange membrane fuel cells (PEMFC) cathode received much for further development to improve the limited performance of the PEMFC [23, 24]. As mentioned above, the nanostructured Pd-based alloys are utilized for enhancing the kinetics on the cathode and hence maximize the efficiency of the ORR [25]. For extending these studies, PdCr@carbon catalysts are prepared by a modified polyol reduction method to enhance the effectiveness of the pure Pd catalysts. The influence of the calcination process on the chemical stability, activity, and

structural parameters of PdCr@carbon catalysts is investigated using XRD, TEM, cyclic voltammetry (CV), and electrochemical polarization tests.

2. Experimental details

$(\text{NH}_4)_2\text{PdCl}_4$ and $\text{CrCl}_2 \cdot 6\text{H}_2\text{O}$ are provided from DAEJUNG Chemicals & Metals CO., Ltd., of purity of 98.5%. Ionic poly (diallyl dimethyl ammonium) (PDDA) (10,000 g/mol) and ethylene glycol are purchased from SAMCHUN Pure Chemical CO., Ltd., of purity of 99.5%. NaBH_4 and carbon (Vulcan XC 72R) are provided from KANTO Chemical CO., Inc., of purity of 92%. All the mentioned chemicals were analytic grade and utilized without further purgation.

The $\text{Pd}_{68}\text{Cr}_{32}$ on the carbon-supported surface are fabricated via a developed polyol reduction method. The proposed amounts of Pd and Cr salts are weighted to form 0.1 g of PdCr and then are mixed in deionized water. On another side, 30 ml of PDDA is mixed with 30 ml of ethylene glycol and then the mixture is sonicated for $\frac{1}{4}$ h. A 40 ml of ethylene glycol refluxed at 403 K using a magnetic stirrer. Then, the prepared solution of PDDA and PdCr is added dropwise to the ethylene glycol under stirring condition 10 times with the desired amounts to giving an atomic ratio of PDDA:PdCr = 7:1. The stirring process is performed for 1 h at least, and the reduction process of Pd and Cr ions took place by adding a solution that was composed of 0.2 g NaBH_4 in 40 ml of the deionized water. During the preparation process, the solution color was changed gradually from yellow to black which reveals the formation of PdCr. More details about the preparation method applied for preparing PdNi nanoalloy available elsewhere [22].

For the formation of PdCr@carbon, a proposed quantity of carbon (Vulcan XC 72R) was mixed into the prepared PdCr solution, and then stirred using a magnetic stirrer for 2 h at 403 K. After that, the mixture was cool down to ambient temperature overnight. The clay slurry was purified, washed with water and ethanol, and dried in a vacuum oven at 343 K. For studying the influence of the heat-treatment on the structural and hence the catalytic activity, the prepared alloy was calcined at 573 K, 773 K, and 973 K in the gas mixture of 10% H_2 -90% Ar for 3 h, followed by cooling to room temperature. On another side, the influence of calcination duration was performed for various times up to 5 h at calcined temperature equals 573 K.

Philips Pan analytical X-ray diffractometer is used to investigate the crystal structures of the as-prepared and calcined PdCr@carbon catalysts. More details concerned the XRD conditions and analysis for other materials available elsewhere [15]. The nominal concentration of Cr and Pd in the formed catalyst is estimated using the ICP-AES technique. The nanostructures of PdCr such as particle distribution, shape, and average size are quantitatively determined using TEM model JEOL 2010F, and the measurements carried out at 200 kV.

The CV and ORR measurements are performed using three electrodes setup and the potential is supplied using a Biologic VSP potentiostat. In the electrochemical measurements Pt mesh, a glassy carbon substrate of 5 mm in diameter, and Ag/AgCl is used as the counter, working, and working electrodes, respectively. Before starting the measurements, the PdCr@carbon catalyst is deposited on the polished glassy carbon to form a monolayer of the catalyst and then dried for ¼ h at 333 K. The CV measurements carried out in N₂-purged 0.1 M HClO₄ and the scan performed in the potential range between -0.2 and 1 V with a step scan of 50 mV s⁻¹. Then the ORR measurements were done between -0.2 and 0.8 V with a step scan of 50 mV s⁻¹ and the used solution is O₂-saturated 0.1 M HClO₄. All electrochemical measurements are repeated three times to assure the reproducibility of the obtained results.

3. Results and discussion

The ICP-AES test was applied to check the atomic percentage ratio of the individual elements in the PdCr nanoalloy. It was found that the ratio between Pd and Cr is 68:32.

The influence of the calcination temperature and calcination time on the structural parameters carried out by the XRD technique. **Fig. 1a** shows the XRD patterns of as-prepared, and calcined PdCr@carbon samples at various calcination temperatures (573, 773, and 973 K) for 3 h. Generally observed, the charts reveal five dominant peaks belongs to the fcc crystal structure of the Pd phase following the JCPDS Card 46-1043 [15]. Two other peaks are observed the tetragonal crystal structure belongs to the PdCr phase and their Miller indices summarized in **Table 2**. The observed peaks belong to the diffraction from planes (111), (200), (220), (311), and (222). Also, there are some small and broad peaks related to the tetragonal PdCr phase which agrees with Ref. [26]. Such peaks are observed for as-prepared and calcined samples at 573 K but disappeared

from the XRD charts for the PdCr samples calcined at a greater temperature such as 773 and 973 K. Besides, a broad peak is observed at 2θ equals 25° and this diffraction peak belongs to the Miller indices of (002) of the hcp crystal structure of the carbon Vulcan. Moreover, it was observed that there is an overlapping peak for both PdCr and Pd phases for the as-prepared PdCr@carbon. The formation of the PdCr@carbon alloy is emphasized by the existence of the diffraction peaks observed in the XRD charts that belong to the fcc and tetragonal phases of Pd and PdCr, respectively. Compared to the crystal structure of pure Pd, the ligament, and average crystallite size reduced, meanwhile the surface strain enhanced [14]. One of the diffraction peaks ($2\theta = 33^\circ$) that related to the fcc crystal structure phase perfectly disappeared for samples calcined at 973 K (**Fig. 1a**). Such behavior could be attributed to the formation of a Pd-rich phase over the surface. This observation is well following our previous study of the PdNi alloy [22].

Fig. 1b presented the XRD charts for PdCr@carbon samples that calcinated at 573 K for various calcination duration. For this objective, the structural behavior of PdCr@carbon at the optimized calcination temperature (573 K) is performed at different times (1-5 h). It was deduced that the calcination for 1 h leads to wide diffraction peaks and their position is shifted to greater 2θ compared to the as-prepared samples. The shift in peak positions could be attributed to the change in the lattice parameters of the nanocatalyst. In other words, the prepared catalyst shows a significant response to the calcination process, which resulted in a reduction in the particle as well as crystallite size and hence an expected higher surface area. An improvement in the particle homogenization was observed for samples that calcined for 4 and 5 h. The evaluated structural parameters due to the calcination process are summarized in **Tables 1 & 2**. The active surface area (S) in m^2g^{-1} was estimated from the following equation ($S = \frac{6000}{d\rho}$) that valid for the spherical particles [27], where d is the crystallite size estimated from the (111) diffraction peak in the XRD charts depicted in **Fig. 1**, and it was computed from the Scherrer equation [28], while ρ is the density of the PdCr and equals $\sim 10.6 \text{ g.cm}^{-3}$. The estimated value of S is $58.74 \text{ m}^2/\text{g}$ for the as-prepared PdCr and was decreased to $15.12 \text{ m}^2/\text{g}$ as the calcined temperature increased up to 973 K. The dislocation (δ) and the microstrain (μ) is estimated from $\delta = (\frac{1}{d^2})$, and $\mu = (\frac{\lambda}{d\cos(\theta)} - \beta_{hkl}) \frac{1}{\tan(\theta)}$, respectively, where β_{hkl} is the full width at half the maximum

intensity of the reflection peak. Both the dislocation and microstrain is decreased with increasing the calcination temperature and the maximum microstrain (2.1×10^{-2}) was observed for sample calcined at 573 K for 3 h. The numerical values of the dislocation density were decreased from $10.72 \times 10^{15} / \text{m}^2$ to $7.1 \times 10^{14} / \text{m}^2$ as the PdCr samples calcined to 973 K. The greatest value for S and dislocation density are observed for the PdCr sample that calcined at 573 K for 1 h, and their numerical values are $70.58 \text{ m}^2/\text{g}$, and $15.47 \times 10^{15} / \text{m}^2$, respectively. According to the above discussion, we can conclude that the optimum calcination temperature should be performed at 573 K for 3 h.

The morphologies of as-prepared and calcined PdCr@carbon catalysts were investigated using the high-resolution transmission electron microscopy (HR-TEM) as shown in **Figs. 2 & 3**. **Fig. 2** show the selected TEM images for as-prepared and calcined PdCr@carbon samples at 573, and 773 K for 3h. It is generally observed, the formed nanoparticles are highly ordered while some of the particles are agglomerated. The average estimated particle size for all the calcined samples lie between 30 and 60 nm. The TEM image reveals that the particles have a spherical shape with some aggregation with various sizes of 40-45 nm, for the as-prepared samples **Fig. 2a**. The shape of the observed particles for the as-prepared PdCr@carbon samples takes the triangle and square forms. It could be noticed that the estimated particle size from the TEM images is greater than those estimated from the XRD. The difference could be attributed to the internal polycrystal grain boundaries that aren't exposed [22]. **Fig. 2b** shows the TEM image of the PdCr sample calcined at 573 K for 3 h which reflects a good dispersion and some agglomeration of the small particles. The particle size of small particles increased from ~30 to ~45 nm as the calcination temperature increased from 1h to 5h, while the larger particle sizes remain constant at 60 nm for all calcination time. Besides, by the calcination process (temperature and time) the shape of the particles transforms from a triangle and square shape to a spherical shape. Ping *et al.*, [19] have prepared the PdCr catalysts in different atomic ratios on coal surfaces for hydrogen production. It was reported that a smaller particle size of Pd (4.66 nm) formed by the reduction of PdCr on carbon substrate [29]. Meanwhile, a larger particle size of 6.8 nm was formed in the Cr@Pd core-shell over the multi-walled carbon nanotubes assisted by NaBH_4 as a reducing agent [30].

The CV scans (CVs) were performed to evaluate the hydrogen adsorption/desorption potentials of the as-prepared and calcined PdCr@carbon. **Fig. 4a**, and **4b**, show these CVs for the investigated PdCr@carbon samples calcined at

various temperatures, and 573 K for various times, respectively. The deduced value of adsorption/desorption potentials was found to depend on the calcination temperature and time and hence the particle size. Smaller values, between -0.19 and -0.11 V, was observed at lower calcined temperature and minimized for 3h calcination. The lower value of adsorption/desorption potentials resulted in higher electrocatalytic activity. The minimum value of adsorption/desorption potentials and hence the greater electrocatalytic activity was corresponding to the prepared samples with the smallest particle size. Besides the potential required for oxidation (positive side) and/or reduction process (negative side) is a bit shifted to the positive potential. Such observations confirm that the samples calcined at lower temperatures show a greater enhancement in the electrocatalytic activity and this is attributed to the chemisorption of oxygenated on the Pd sites that formed above 0.5 V.

Figs. 5a and **5b** show single scan voltammograms for PdCr@carbon catalyst calcined at different calcination temperatures, and 573 K for different calcination times, respectively. It is generally observed that higher ORR activity is detected for PdCr@carbon that calcined at 573 K. The observed higher value of the ORR activity could be attributed to the formation of smaller particle size and hence a higher surface area as can be seen in **Table 1**. The calcination at lower temperatures leads to the migration of Pd atoms to the alloys surface, and this because of the great possibility of segregation energy between Pd and Cr [25]. The investigated PdCr alloy is composed of two different elements one of them (Pd) has an approximately empty d-orbital while the other element (Cr) has nearly a fully occupied d-orbital [31]. Therefore, the coupling of d-orbital between them will reduce the Gibbs free energy of the electrons and leads to an improvement in the ORR activity. Besides, the substitution of Pd with Cr atoms could affect the electronic structure of the new product, and accordingly, the kinetics reaction for the ORR and reduction efficiency will increase. For the samples that calcined at 573 K for various times, the ORR activity decreased as the duration of calcination was increased. The decrease in the ORR activity can be attributed to the increased in the particle size and hence the reduction of surface area for samples calcined for longer time

4. Conclusions

In summary, PdCr@carbon nanoparticles were formed by the modified polyol reduction method to be used as an efficient catalyst for the PEMFCs. The crystal structure and morphology of PdCr@carbon are controlled by the calcination temperature and time. The calcination process leads to the formation of the fcc Pd phase together with the tetragonal PdCr phase. The average crystallite size is increased while the active surface area, dislocation density, and microstrains of PdCr are decreased as the calcination temperature and/or time increased. The average particle size of 20-50 nm is obtained and the highest surface area was observed for samples calcined at 573 K for 3 h. Therefore, the higher ORR activity was achieved for samples calcined at 573 K for 3h. The formation of such small particle sizes reduces the potential range required for the adsorption/desorption of hydrogen and hence improving the electrocatalytic reaction activity.

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Figures

Figure 1

XRD charts of as-prepared and calcined PdCr@carbon (a) at different calcined temperatures and (b) at 573 K for different calcination times.

Figure 2

TEM images of carbon-supported PdCr@carbon catalyst for (a) the as-prepared sample, and samples calcined for 3 h, at (b) 573 K, and (c) 773 K.

Figure 3

TEM micrographs of the carbon-supported PdCr@carbon catalyst calcined at 573 K for (a) 1 h, (b) 2 h, (c) 4 h, and (d) 5 h.

Figure 4

Cyclic voltammetry (CV) of PdCr@carbon catalysts calcined (a) at various calcination temperatures for 3 h, and calcined (b) at 573 K for various calcination durations.

Figure 5

Single scan voltammograms (I-E) curves for PdCr@carbon catalyst calcined (a) at various calcination temperatures and (b) at 573 K for various calcination durations.