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# Preparation of Pt-based ternary catalyst as cathode material for proton exchange membrane fuel cell by solution route method

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## ABSTRACT

In this research, Pt-based ternary catalysts for proton exchange membrane fuel cell (PEMFC) have been successfully prepared by the solution route method. This type of catalyst was claimed to improve the activities of oxygen reduction reaction (ORR). The ternary catalyst was prepared using 10% platinum, 5% cobalt, and 5% chromium by weight support on untreated and treated carbons by reduction with $NaBH_4$ at room temperature. The FTIR spectra showed a new functional group as carboxyl group on treated carbon using $H_2O_2$. The XRD patterns for both carbon samples confirmed platinum and carbon phases in the products. The EDS spectra detected platinum, cobalt, chromium, oxygen and carbon atoms in the prepared catalysts. The XAS patterns revealed that the products were mixed Pt–CoO–$Cr_2O_3$ catalysts. The SEM and TEM images showed more dispersion of catalyst on the treated carbon support surface than on the untreated carbon support. Particles size were 3.97 nm for untreated carbon and 1.93 nm for treated carbon. Finally, the electrochemical property was tested by CV technique. It indicated that Pt–CoO–$Cr_2O_3$/C catalyst supported on treated carbon exhibited the highest performance among the prepared ternary alloy catalysts.

## 1. Introduction

The proton exchange membrane fuel cell (PEMFC) is a green technology developed as a source of continuous clean energy. In general, platinum supported on a carbon catalyst was used as the anode and cathode materials. At the anode, platinum will catalyze the hydrogen dissociation into protons and electrons. At the cathode, platinum will catalyze oxygen dissociation. Using platinum catalyst at the cathode, the oxygen reduction reaction (ORR) was reported to be a two electron mechanism, which produced hydrogen peroxide and destroyed the electrode surface. Moreover, platinum catalyst is an expensive reagent [1,2].

In recent years, binary or ternary phase platinum compounds were considered as new catalysts for PEMFC because the reaction from these catalysts prevented the cathode surface from exposure to hydrogen-peroxide and obtained higher electrochemical activity than platinum only catalysts. However, the most important aspect of using Pt ternary compound was that a four-electron path way was obtained by these types of catalyst [2]. The transition metals such as Cu, Ni, Co, Cr, and Cu were reported to be second and third metals added to platinum to prepare low content platinum ternary compounds [3–6]. The platinum-base ternary compounds such as Pt–Co–Cr [7], Pt–V–Fe [8], Pt–Co–Cu [9] and Pt–Cu–Fe [5] have higher electro-activity than platinum-binary compound because of higher kinetic parameters [9]. Catalysts preparation on carbon support was commonly performed by adding the metal precursors to a suspension of already prepared platinum on carbon support (two steps method) followed by thermal treatment at high temperature [10]. Another preparation method was the co-precipitation of platinum, metal 1 and metal 2 together (one step method) and treatment at high temperature [11]. However the particle size obtained from this method was large and required high energy. The solution route method can be used to synthesize nanoparticles of material with size smaller than those from the heat treatment process [12–15]. Moreover, preliminary introduction of functional groups on the carbon surface by treated with hydrogen peroxide was consequences in good dispersion of metal particles on carbon support [16,17].

In this research, the functional groups on the surface of carbon were as well modified by treatment with hydrogen peroxide. After that, the Pt–Co–Cr ternary catalysts supported on carbon were synthesized by solution method using $H_2PtCl_6{\cdot}xH_2O$, $Co(NO_3)_3{\cdot}6H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$ as metal sources and $NaBH_4$ as a reducing agent. Untreated and treated carbons were applied as supporters

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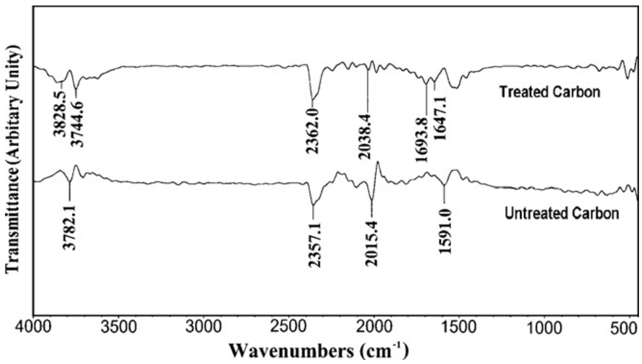

**Fig. 1.** FTIR spectrum from treated carbon and untreated carbon.

to investigate the effect of carbon surface modification on metals dispersion.

## 2. Experimental

In this research, the solution route method was used to synthesize Pt–Co–Cr catalysts supported on both treated carbon and untreated carbon. All the chemicals of analytical grade were used without further purification.

The detail of experiment was as follows; 20% by weight of Pt–Co–Cr, with 2:1:1 mole ratio, supported on 80% by weight of carbon was synthesized by firstly cleaning carbon (Vulcan XC-72) with 2 M $H_2SO_4$ (J.T. Baker 96.3%) at 60 °C for 2 h. After washing with deionized water, it was cleaned with 1 M KOH (BDH 85.0%) at 60 °C for 2 h. After washing out the hydroxide ions, cleaned carbon was treated in 8 N $H_2O_2$ (NCG 50%) for 48 h at room temperature. Then, it was filtered, washed with deionized water, and dried in an oven. The treated carbon was characterized by Fourier transform infrared spectroscopy (FTIR, Nicolet 510). Then, this treated carbon was added into ethylene glycol and pH adjusted to be 9 by KOH solution (BDH 85.0%). Then, it was sonicated for 15 min. After that, stoichiometric amount of $H_2PtCl_6{\cdot}xH_2O$ (Sigma, purum 38%), $Co(NO_3)_3{\cdot}6H_2O$ (AJAX 98%), and $Cr(NO_3)_3{\cdot}9H_2O$ (MERCK 98%) was added in to the carbon mixture. Finally, stoichiometric amount of powder $NaBH_4$ (MERCK 98%) was added for a reduction process to occur and the reaction was allowed to proceed at room temperature for 12 h. The final powder was filtered, washed with methanol and dried in oven for 12 h. The same procedure was applied to prepare Pt–Co–Cr supported on untreated carbon.

The prepared catalyst was further physically characterized by powder X-ray diffraction (XRD, Siemen D500/D501, Cu $K_\alpha$ ($\lambda$ = 1.54 Å) Ni filter, $2\theta$ = 10–80° with scan rate of 0.02°/s for phase identification. Scanning electron microscopy (SEM, JEOL JSM-5910LV)) equipped with energy dispersive spectroscopy (INCA, The Microanalysis Suite Issue-16) was then applied for morphology study and for qualitative and quantitative analyses of elements presented in the samples. Transmission electron microscopy (TEM, JEOL JEM-2010) was used for the size and particle dispersion determination on the carbon supports. X-ray absorption spectrometry (XAS, beam line 8 at the synchrotron light research institute, Thailand) was carried out to identify oxidation states of metals and local structure on carbon supports.

Electrochemically testing by cyclic voltammetry technique (BAS CV-50W Voltammetric analyzer) was performed finally. A glassy carbon disk, Ag/AgCl and Pt wire as working, reference and auxiliary electrodes with 1.00 M $H_2SO_4$ as electrolyte. To prepare the working electrode, 10 mg of prepared catalyst was sonicated in a mix of 0.5 ml of deionized water and 0.06 ml of 5% Nafion solution (Electrochem, Inc.) for 30 min. After that, 5 μl of the homogenous solution was dropped on a 5 mm diameter glassy carbon disk electrode (glassy carbon area: 0.196 cm$^2$) and allowed to dry at 70 °C in an oven for 30 min. Then, 5 μl of 5% Nafion solution was dropped on the glassy carbon surface again and dried at 70 °C in an oven for 10 min. Cyclic voltammograms were operated between 0 and 1.2 V (vs. Ag/AgCl) at a scan rate of 20 mV s$^{-1}$ for 30 cycles.

## 3. Results and discussions

The modified functional groups on the treated carbon surface were analyzed compared with untreated carbon. They were characterized by FTIR as shown in Fig. 1. It can be seen that the untreated carbon shows peaks at 2357, 2015 and 1591 cm$^{-1}$ corresponding to the vibration of $-C{\equiv}C-$, $-C{=}C{=}C-$ and $-C{=}C-$, respectively. By comparison to carbon treatment by hydrogen peroxide, peaks were detected at 2362, 2038 and 1647 cm$^{-1}$ corresponding to the vibration of $-C{\equiv}C-$, $-C{=}C{=}C-$ and $-C{=}C-$, respectively, similar to the untreated carbon. However, a new small peak at 1693 cm$^{-1}$ was additionally detected, which was identified as carboxylic group ($-C({=}O)-O-$). The appearance of this functional group was due to hydrogen peroxide which was a strong oxidizing agent and can oxidize the carbon–carbon bond on carbon surface to carboxylic group. This carbolic group, which is a negatively charged functional group, can improved the formation of Pt-based ternary catalysts on carbon due to electrostatic interaction between a metal ion, which is a positive charge, and carbolic group (negative charge).

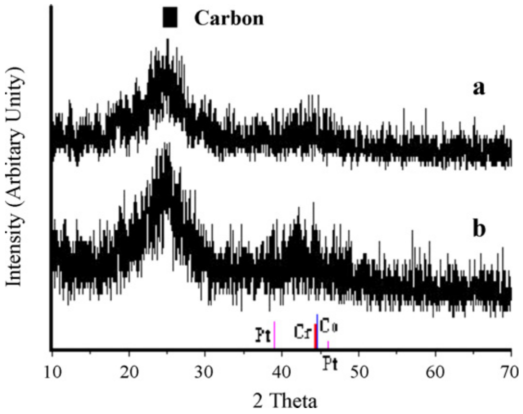

**Fig. 2.** Powder XRD patterns of (a) Pt-based ternary catalyst on untreated carbon and (b) Pt-based ternary catalyst on treated carbon.

**Table 1**
Percent weights of cobalt, chromium, platinum, oxygen and carbon of Pt-based ternary catalyst on untreated and treated carbons from EDS.

| Carbon | Element (wt%) | | | | |
|---|---|---|---|---|---|
| | C | O | Pt | Co | Cr |
| Untreated | 86.60 | 5.51 | 5.28 | 1.73 | 0.88 |
| Treated $H_2O_2$ | 82.71 | 5.18 | 6.65 | 3.38 | 2.08 |

The XRD patterns of Pt-ternary catalysts supported on carbon untreated and treated by hydrogen peroxide are shown in Fig. 2. They show a broad peak at $2\theta$ = 25.34° corresponding to (0 0 2) plane of carbon (JCPDS No. 00-001-0640). However, the metals peaks were unclearly observed in the XRD patterns, which might be because of a small particle size effect and the low amount of metals. Therefore, the electron diffraction and X-ray absorption spectrometry (XAS) were then used identify the occurrence of these metals.

The particle size distribution of Pt-based ternary catalyst on untreated and treated carbons was investigated by SEM in backscattered electron mode (BSE) as shown in Fig. 3. In BSE image, the bright spots corresponded to metal with high atomic number such as Pt, Co and Cr. Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image. BSE image of Pt-ternary catalyst on treated carbon (Fig. 3b) shows relatively higher distribution of catalyst metals than those on untreated carbon. Their actual particle size and microstructure of the prepared catalysts were further investigated by the transmission electron microscopy (TEM) technique.

The qualitative and quantitative analyses of elements on both carbon supports were detected by energy dispersive X-ray spectroscopy (EDS) as shown in Table 1. It was noted that the intensities of EDS spectra of Pt, Co and Cr metals on treated carbon were higher than that of those from untreated carbon which corresponding to higher amounts of all metals on treated carbon than on untreated carbon.

Fig. 4 shows the TEM images of Pt-based ternary catalyst on untreated and treated carbons. It was found that the catalysts were

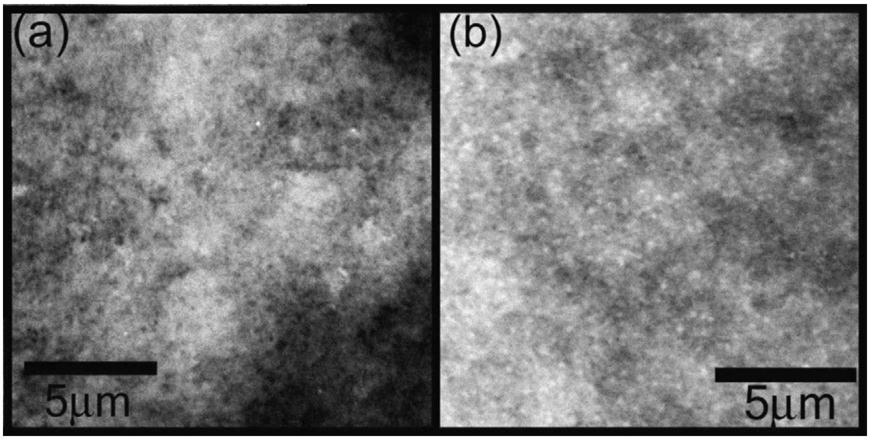

**Fig. 3.** Black scattered SEM images of (a) Pt-based ternary catalyst on untreated carbon and (b) Pt-based ternary catalyst on treated carbon.

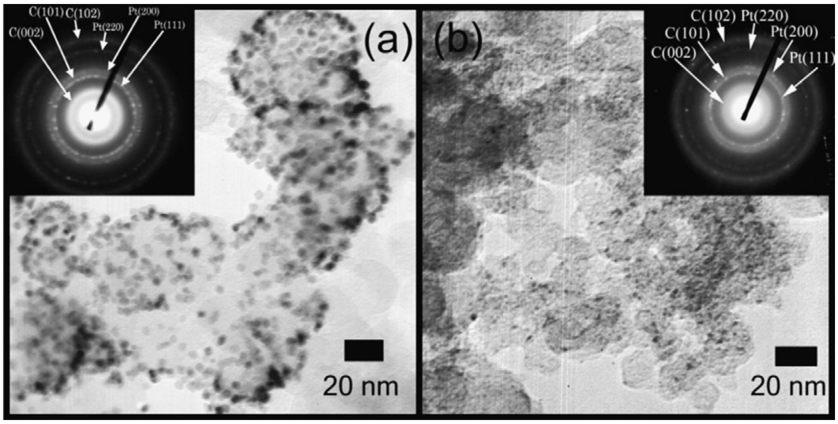

**Fig. 4.** TEM images and their corresponding SAED patterns of (a) Pt-based ternary catalyst on untreated carbon and (b) Pt-based ternary catalyst on treated carbon.

nanoparticles on untreated carbon (Fig. 4a) with average particle size of 3.97 ± 0.63 nm and good dispersive sphere nanoparticle on treated carbon (Fig. 4b) with particle size of 1.93 ± 0.35 nm. In general, the catalyst with a good uniform distribution and smallest nanoscale will improve the fuel cell performance due to high surface area. The selected area electron diffraction (SAD) patterns were inserted in the TEM images. The SAD pattern of both as-synthesizes samples can be indexed to (0 0 2), (1 0 1) and (1 0 2) planes of carbon and (1 1 1), (2 0 0) and (2 2 0) planes of platinum.

The XAS technique was used to identify Pt-based ternary catalyst on untreated and treated carbons using Co, CoO and $Co_3O_4$ as cobalt standard and Cr and $Cr_2O_3$ as chromium standards. The XANS and EXAFS spectra for sample and cobalt standards are shown in Fig. 5. It confirmed that Co in the sample was CoO compound because of similar spectrum characteristic between CoO standard and sample. Fig. 6 shows the XANS and EXAFS spectra of samples and chromium standards. Both samples shown similar spectrum to $Cr_2O_3$ standard. It can be concluded that Cr contained in the sample was $Cr_2O_3$ compound. The existence of oxide phase might be explained as because chromium ion (+3) and cobalt ion (+2) are the most stable oxidation state and preparation process was conducted in an air atmosphere [17].

The electroactivities of Pt-based ternary catalyst on untreated and treated carbons were investigated by cyclic voltammogram (CV) with comparison of commercial Pt/C catalyst from Fuel Cells Scientific. The CV spectra are shown in Fig. 7. They indicated a maximum current and potential at $7.277 \times 10^{-5}$ A and 564 mV for commercial Pt/C grade, $8.423 \times 10^{-5}$ A and 539 mV for catalyst on untreated carbon and $9.417 \times 10^{-5}$ A and 534 mV for catalyst on treated carbon at the same condition. It can be seen that catalyst on treated carbon showed a higher current of 1.12 and 1.29 times that over of catalyst on untreated and commercial Pt/C grade. Table 2 showed the Pt loadings of commercial Pt/C catalyst and Pt-based ternary catalyst on untreated and treated carbons on the glassy carbon disk. It can be seen that the Pt loading on the glassy carbon disk was 0.100 mg/cm$^2$ for commercial Pt/C grade, but only 0.03 mg/cm$^2$ for both Pt-based ternary catalyst on untreated and treated carbons. It can be concluded that the Pt-based ternary catalyst on treated carbon provided relatively higher current than commercial catalyst with lower Pt loading. Therefore, the ternary catalysts Pt–CoO–$Cr_2O_3$ supported on treated carbon can be considered as a candidate catalyst for PEMFC.

**Table 2**
Weight catalysis loading on the glassy carbon disk.

| Sample | Weight catalysis loading (mg/cm$^2$) |
|---|---|
| 20% Pt/C (Fuel Cells Scientific) | 0.1 |
| Pt:CoO:$Cr_2O_3$ on untreated carbon[a] | 0.027:0.011:0.013 |
| Pt:CoO:$Cr_2O_3$ on treated carbon[a] | 0.034:0.022:0.031 |

[a] Weight calculation from EDS data.

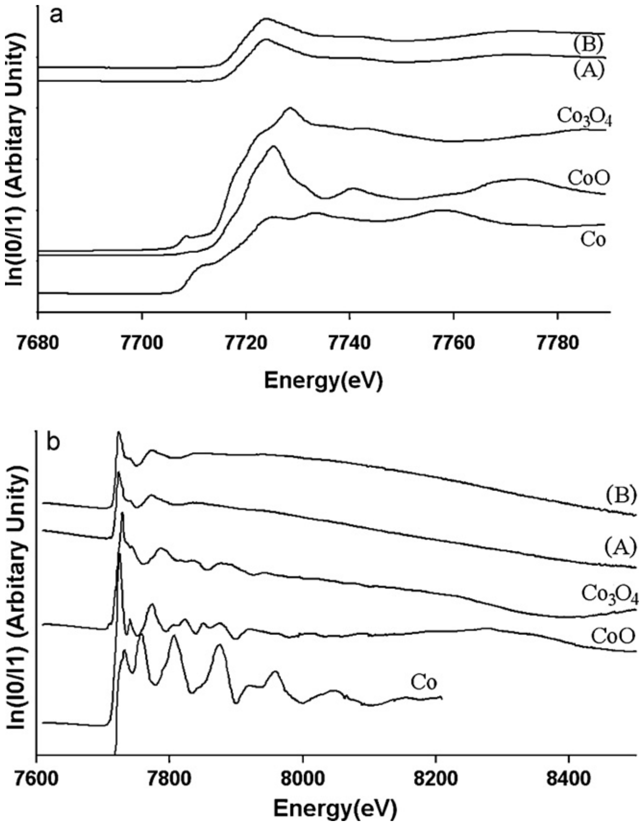

**Fig. 5.** The XANS (a) and EXAFS (b) spectrum of cobalt in catalyst samples on untreated carbon (A) sample and catalyst on treated carbon (B) compared with standard spectrum of cobalt metal and cobalt oxides.

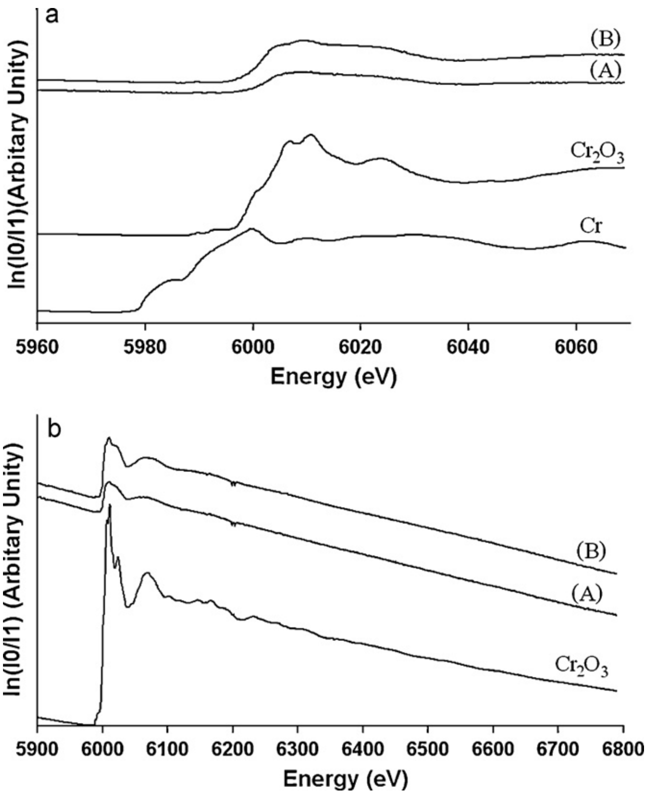

**Fig. 6.** The XANS (a) and EXAFS (b) spectrum of chromium in catalyst samples on untreated carbon (A) sample and catalyst on treated carbon (B) compared with standard spectrum of chromium metal and chromium oxides.

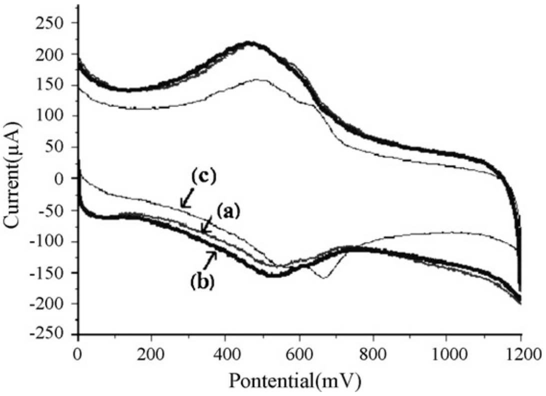

**Fig. 7.** Cyclic voltammetry spectrum of (a) Pt-based ternary catalyst on untreated carbon sample, (b) Pt-based ternary catalyst on treated carbon and (c) 20% Pt/C catalyst standard from Fuel Cells Scientific.

## 4. Conclusions

Pt-based ternary catalysts supported on untreated and treated carbons can be synthesized by the solution route method using $NaBH_4$ as a reducing agent. Measurements indicated that Pt-based ternary catalysts on treated carbon show small particle size (≈2 nm) with good dispersion and Pt–CoO–$Cr_2O_3$ nanoparticles on treated carbon surface, which lead to the highest electrochemical performance compared with Pt–CoO–$Cr_2O_3$ catalysts on untreated carbon and commercial Pt/C catalyst.

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