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Research article

Silver and Silver Alloy on Carbon-supported Catalysts for Cathodes in Proton Exchange Membrane Fuel Cell and Direct Ethanol Fuel Cell

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Abstract: This research was focused on the synthesis of 20 %wt silver, silver platinum alloy, and silver-copper alloy catalysts on carbon Vulcan XC-72 supporter for proton exchange membrane fuel cell (PEMFC) and direct ethanol fuel cell (DEFC) cathode using sodium borohydride method. Herein, the ratio of silver and platinum or copper sources was 1:1 by weight. The obtained catalysts were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM), and the electro-activity performance was investigated on single-cell testing. XRD and TEM results confirmed the catalytic products of the Ag metal, AgPt alloy, and silver copper oxide ($Ag_xCu_{2-x}O$). Therefore, the particle size of the catalytic 20%wt AgPt/C was observed in the smallest size of about 4.71 ± 1.03 nm. The catalyst was selected for PEMFC and DEFC cathode testing. It showed high power density of 14.68 and 1.26 $W/cm^2.g_{(M)}$, respectively.

Keywords: Silver-based alloy; Cathode catalyst; Proton exchange membrane fuel cell, Direct ethanol fuel cell

1. Introduction

The proton exchange membrane fuel cell (PEMFC) and direct ethanol fuel cell (DEFC) are green technologies developed for continuous clean energy. Platinum supported on carbon catalyst was generally used as anode and cathode materials. Platinum will catalyze the hydrogen or ethanol dissociation into protons and electrons at the anode. After that, protons travel through the polymer electrolyte membrane from the anode to the cathode, where electrons travel along an external load circuit to the cathode side. At the cathode, platinum will catalyze the dissociation of oxygen. The electrons recombine with the protons and oxygen to form pure water as the reaction byproduct. Using a platinum catalyst at the cathode, the oxygen reduction reaction (ORR) was reported to be two electrons, producing hydrogen peroxide and destroying the electrode surface. Moreover, the platinum catalyst is an expensive reagent [1, 2]. Cathode catalysts such as platinum and non-platinum alloys have replaced pure platinum catalysts. This research focuses on silver and silver alloys because catalysts do not agglomerate after a long

operation. It has properties similar to platinum (same group of the periodic table and same face center cubic crystal structure) but at a much lower cost [3, 4]. Silver alloy catalysts such as CuAg/C [5], AgCu/C [6], and PtAg/C [7, 8, 9] have higher electro-activity than platinum catalysts. The catalyst for the cathode fuel cell should have nano-size particles with a good dispersion on the carbon supporter. To obtain a nano-sized product, many processes, such as heat treatment in hydrogen gas and nitrogen gas, are used [10, 11]. However, this method requires high energy and a complicated procedure. This research uses sodium borohydride ($NaBH_4$) to reduce metal ions in solvent to form metal or metal alloy because of its strong reductive ability [12, 13, 14]. Moreover, good dispersion of catalysts on carbon support will be obtained using modified surface carbon with hydrogen peroxide (H_2O_2) [15, 16]. In this research, the functional groups on the carbon surface were modified by being treated with hydrogen peroxide. After that, the Ag, AgCu, and AgPt catalyst supported on treated carbon was synthesized by the $NaBH_4$ method using $AgNO_3$, $Cu(NO_3)_2{\cdot}3H_2O$ and $H_2PtCl_6{\cdot}xH_2O$ as metal sources and ethylene glycol as a solvent

2. Materials and Methods

2.1 Carbon supporter treatment

H_2O_2 was used to modify the carbon surface. First, Carbon Vulcan XC-72 (Fuel Cell Store) was stirred in H_2SO_4 (97.5-98.5%, RCI Labscan). Then, washed with deionized water and stirred in KOH (85.0%, Ajax Finechem). Then, it was washed and stirred in H_2O_2 (50%, World Chemical Group) for 48 hours at room temperature. Finally, it was filtered, washed with deionized water, and dried in the oven. Fourier transform infrared spectroscopy (FTIR, FTIR-8900, Shimadzu) characterized functional groups of the carbon surface.

2.2 Synthesis of silver and silver-alloy

Twenty percent by weights of silver, silver-platinum alloy, and silver-copper alloy catalysts supported on carbon Vulcan XC-72 were prepared using $NaBH_4$ reducing agent. The ratio of silver to other metals was varied as 1:1 by weight. The treated carbon and metal sources ($AgNO_3$ 99.8%, RCI Labscan, $Cu(NO_3)_2{\cdot}3H_2O$ 99.5%, QRëC, and $H_2PtCl_6{\cdot}xH_2O$, Sigma-Aldrich) were added into ethylene glycol (99.5%, LoBa Chemie). The $NaBH_4$ (97.0%, LoBa Chemie) was added to the mix solutions. The reaction was stirred for 24 hours. Finally, the black product was filtered, washed with ethanol (95%, World Chemical Group), and dried in an oven to obtain the catalyst samples (20 %wt Ag/C, 20 %wt AgCu/C, and 20 %wt AgPt/C). The prepared catalysts were characterized by X-ray diffraction (XRD, RigaKu, Cu K_α (λ 1.54)), Scanning Electron Microscopy (SEM, JSM-5910LV, JEOL) equipped with Energy Dispersive Spectroscopy (EDS, The Microanalysis Suite Issue-16, INCA) and Transmission Electron Microscopy (TEM, JEM-2010, JEOL) techniques.

2.3 Single-cell testing

A single-cell testing station investigated the electrochemical performance of all catalysts acting as PEMFC and DEFC cathode (FCED, P200, APFCT). Catalyst-coated membrane (NR-212, Fuel Cell Store, as electrolyte for both fuel cells) was prepared using the commercial 20 %wt Pt/C (Fuel Cell Store, Pt/C_std) for the anode side and prepared catalyst for the cathode side. One membrane side was sprayed with an anode catalyst area of about 3 cm x 3 cm and nearly 0.4 mg/cm^2 for catalyst loading. Another membrane side was sprayed with a cathode catalyst in the same area. A single-cell testing technique was used to compare the electro-catalyst activity of PEMFC and DEFC. The PEMFC used hydrogen gas on the anode side and oxygen gas on the cathode side. The gas flow rate is 0.5 slpm for both sides. The single cell was operated at room temperature and 1 atm pressure. The DEFC used oxygen gas at the cathode side, and the gas flow rate was 0.5 slpm. At the anode side with 10% ethanol solution, the flow rate was 1.0 Lhr^{-1}, and the temperature was 60 °C. The single cell was operated at 60 °C and 1 atm pressure.

3. Results and Discussion

The modified functional groups on the treated carbon surface were compared with untreated carbon. They were characterized by FTIR, as shown in Figure 1. It can be seen that the untreated carbon's peaks at 3155.3 and 1602.9 cm^{-1} correspond to the vibration of -O-H and -C=C-, respectively. However, they were observed with low intensity. The treated carbon with hydrogen peroxide was detected in the bands at 3396.4, 1652.9, and 1558.4 cm^{-1}, corresponding to the vibration of –O-H, -C=O, and –C=C-, respectively. It also detected the bands at 1440-1395, 1320-1210, and 750-650 cm^{-1} corresponding to the vibration of -C-O, -O-H, and -O-H out of the plane, respectively, confirmed carboxylic group (-C(=O)-O-H). Those functional groups appeared due to hydrogen peroxide, which acted as a strong oxidizing agent [17] and can oxidize the carbon-carbon bond on the carbon surface to carboxylic group [18, 19]. This carboxylic group, a negatively charged functional group, induces the formation of metal alloy catalysts on carbon due to electrostatic interaction between a metal ion and carboxylic group. The catalyst on treated carbon surface with a good uniform distribution and smaller nanoscale than catalyst on untreated carbon because nucleation rate was greater than agglomeration rate of particle [20,21].

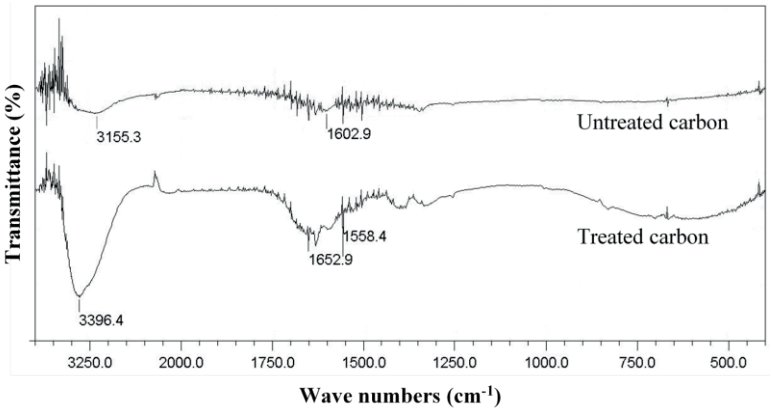

Figure 1. FTIR spectra of treated carbon and untreated carbon

XRD patterns of 20 %wt Ag/C, 20 %wt AgCu/C, and 20 %wt AgPt/C catalysts are shown in Figure 2. All catalysts show the board peak at 2θ ≈ 24° corresponding to the (002) plane of carbon. 20%Ag/C showed the peaks at 2θ = 38.06° (111), 44.21° (200), and 64.45° (220), which corresponded planes of cubic Ag metal with space group *Fm3m* (JCPDS No.00-004-0783). While XRD patterns of the catalytic products from synthetic 20 %wt AgCu/C were identified as $Ag_xCu_{2-x}O$ compound [22, 23], XRD patterns exhibited evidence of the diffraction peaks have shifted to lower 2θ values, the position of (111) plane was closer to silver copper (I) oxide than Ag metal due to copper (I) oxide with the larger hole radius than silver had replaced the silver position with the metals oxide can be oxidized by oxygen in air under $NaBH_4$ solution condition at the ambient temperature is represented in Table 1. The XRD pattern of the catalytic product from 20 %wt AgPt/C, the 2θ position of (111) plane of the sample, was compared with Ag and Pt metals, which were identified as AgPt alloy [8, 24, 25] as shown in Table 1. The characteristic diffraction peaks of AgPt/C catalysts have shifted to higher 2θ values. The position of the (111) plane was closer to Ag alloy than Ag metal because the size of the unit cell from Ag alloy was smaller than that of Ag metal. In addition, platinum had been replaced with a smaller atomic radius than silver at the silver position. After the metals were mixed to form an alloy, the acquired alloy phase provided the different unit cell parameters from the pure metals. In the case of the atomic distance, the distance between the same atomic types appeared further than the distance from the heteroatom by the effect of the atomic force. All XRD patterns are illustrated in Figure 2. The EDS technique confirmed the Ag, Cu, Pt, and O compositions of both silver compound and alloy, as listed in Table 2.

The EDS technique conducted the qualitative and quantitative analyses of elements for all catalysts, as shown in Table 2. The EDS spectra of all catalysts confirmed the presence of respective elements and the amount of carbon, oxygen, and all metals on carbon. The observed oxygen from this technique mostly came from metal oxide. The amount of the observed metals was less than the theoretical metals ratio because of the limitation of this technique and sampling was a small area to use as a representative for all catalysts.

Table 1. Peak positions of the (111) plane between standard and alloy samples

Sample catalysts	2θ for (111) plane
Ag (JCPDS No. 00-004-0783)	38.12
Pt (JCPDS No. 00-004-0802)	39.76
Cu_2O (JCPDS No. 00-005-0667)	36.42
AgPt	38.78
$Ag_xCu_{2-x}O$	37.46

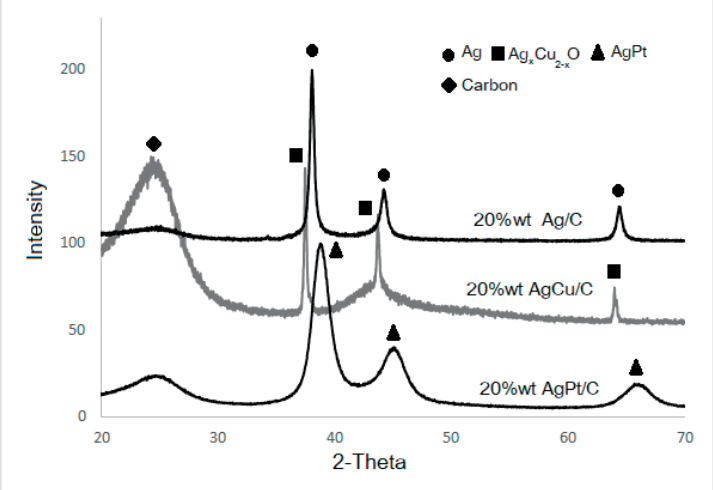

Figure 2. The XRD patterns of silver metal, silver platinum alloy, and silver copper (I) oxide on carbon-supported catalysts

Table 2. Weight percent of silver metal, silver platinum alloy, and silver copper (I) oxide on carbon-supported catalysts from EDS

Synthetic conditions	Element (Wt%)				
	Ag	Cu	Pt	C	O
20 %wt Ag/C	22.71	-	-	77.29	-
20 %wt AgCu/C	10.01	9.15	-	76.92	3.92
20 %wt AgPt/C	15.28	-	2.78	81.94	-

From TEM images of all catalysts shown in Figure 3, the particle sizes of catalysts were observed on the nanoscale with a good dispersion on the carbon surface. The average particle sizes (were used by ImageJ) from Ag/C, AgCu/C, and AgPt/C were 40.67±10.58, 21.99±7.20 and 4.71±1.03 nm, respectively. Figure 3 shows that the smallest particle is the AgPt/C catalyst. The catalyst with the smallest nanoscales will improve the fuel cell performance due to its high surface area [20]. The microstructure of all catalysts was characterized by TEM technique and the phases of products could be confirmed by the selected area electron diffraction (SAED) pattern. In Figure 3, the catalytic products from the synthetic conditions of 20 %wt Ag/C exhibit diffracted ring patterns

of (111), (200), (220), (311), and (222) planes of silver metal. By contrast, the catalytic products from the synthetic condition of 20 %wt AgCu/C exhibit diffracted ring patterns of (111), (200), (220), (311), and (222) planes of silver copper (I) oxide. Moreover, the catalytic products from the synthetic condition of 20 %wt AgPt/C exhibit diffracted ring patterns of (111), (200), (220), and (311) planes of silver platinum alloy. All the SAED results were related to the results from XRD and EDS techniques.

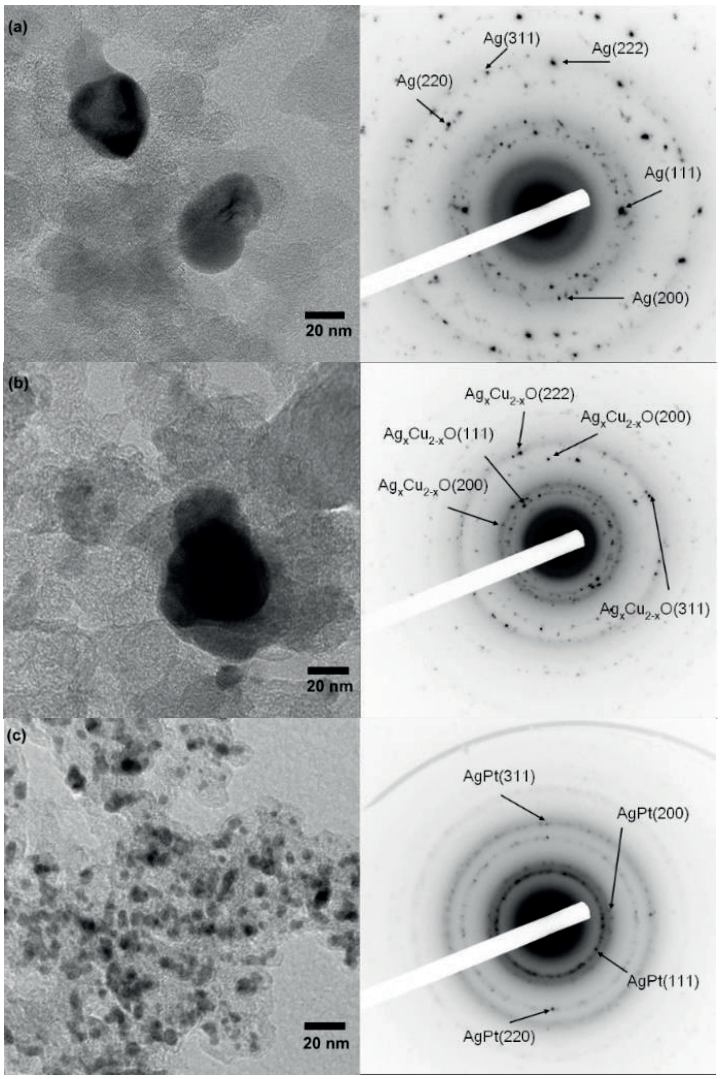

Figure 3. TEM and SADE images of 20 %wt Ag/C (a), 20 %wt AgCu/C (b), and 20 %wt AgPt/C (c) catalysts

Table 3. The power density of silver metal, silver platinum alloy, and silver copper (I) oxide on carbon-supported catalysts

Synthetic onditions	Catalysts at cathode	Particle size (nm)	Power density ($W/cm^2.g_{(M)}$)	
			PEMFC	DEFC
-	Pt/C_std	-	10.32	1.17
20 %wt Ag/C	Ag/C	40.67 ± 10.58	4.99	0.37
20 %wt AgCu/C	$Ag_xCu_{2-x}O$/C	21.99 ± 7.20	5.10	1.19
20 %wt AgPt/C	AgPt/C	4.71 ± 1.03	14.68	1.26

Single cells techniques for PEMFCs and DEFCs (in acidic type) were used to compare the electrocatalysts activity performance between standard and sample cells. The anode catalyst for both cells was commercial 20 %wt Pt/C (Pt/C_std). The cathode catalyst for the standard cell was commercial 20 %wt Pt/C, and sample cells were prepared catalyst (20 %wt Ag/C, 20 %wt AgCu/C, and 20 %wt AgPt/C). The PEMFC was operating at room temperature. The DEFC was operating at 60 °C because a higher temperature lowers the activation loss of the redox reactions, decreases the cell resistance, and enhances the reactant transport [26]. Figures 4(a) and 4(c) show the polarization curve between current density and voltage from single-cell testing of all catalysts for PEMFC and DEFC, respectively. It was found that the 20 %wt AgPt/C catalysts showed higher current density than other catalysts for both testing cells.

The performance curves between current density and power density from PEMFC and DEFC testing of all catalysts are shown in Figure 4b and 4d, respectively. In Table 3, the 20 %wt AgPt/C catalysts showed higher power density than others. The catalysts were 14.68 and 1.26 $W/cm^2.g_{(M)}$ (M as silver or silver alloy catalysts) from PEMFC and DEFC, respectively. The power density of PEMFC was higher than that of DEFC because, on the anode side, PEMFC used hydrogen gas, but DEFC used 10% ethanol solution. Hydrogen gas was faster to decompose with catalyst into positively charged protons and negatively charged electrons than ethanol solution [27,28]. The performance of 20 %wt AgPt/C catalysts was influenced by smaller particles than other catalysts, as confirmed by TEM images. The fine particle catalysts showed better performance because of many active sites on smaller particles compared to catalysts with large particle sizes [29]. In addition, 20 %wt AgPt/C catalysts were reportedly stable after long cell operation with less agglomeration and metals leaching [13]. Therefore, the ORR mechanism of silver platinum alloy formation can break the oxygen bond, leading to completed four-electron reduction without hydrogen-peroxide generation (Eq 1-3) [30,31].

$$AgM + O_2 + e^- \rightarrow AgM\text{-}O\text{-}O^- + H^+ + e^- \rightarrow AgM\text{-}O\text{-}OH^- \quad (1)$$

$$AgM\text{-}O\text{-}OH^- + H^+ + e^- \rightarrow AgM\text{-}O^- + H_2O \quad (2)$$

$$AgM\text{-}O^- + H^+ + e^- \rightarrow AgM\text{-}O\text{-}OH^- + H^+ \rightarrow AgM + H_2O \quad (3)$$

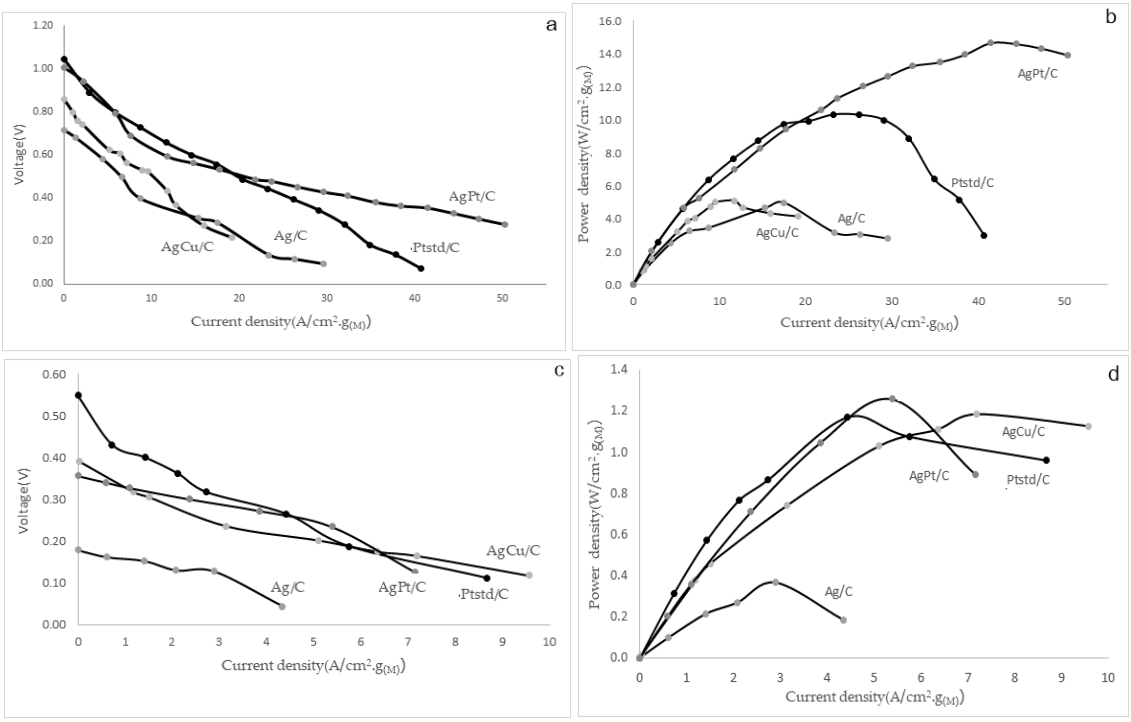

Figure 4. Polarization curves and performance of silver metal, silver platinum alloy, and silver copper (I) oxide on carbon-supported catalysts for PEMFC (a-b) and DEFC (c-d)

4. Conclusions

This research focused on synthesizing 20 %wt silver and silver alloy catalysts on carbon Vulcan XC-72 for PEMFC and DEFC cathode with $NaBH_4$ reduction methods. XRD, TEM, and SAED techniques confirmed the $Ag_xCu_{2-x}O$/C catalyst using equal silver and copper nitrate. Meanwhile, 20 %wt AgPt/C catalyst can easily synthesize due to the high reduction potential of Pt. The particle size of the silver platinum alloy catalyst was observed in a smaller size, around 4.71±1.03 nm. It was selected for the catalytic PEMFC and DEFC cathode testing and showed higher power density than other catalysts. Both testing cells were 14.68 and 1.26 $W/cm^2.g_{@M}$, respectively. This research concluded that 20 %wt AgPt/C catalysts exhibited the highest performance catalyst for PEMFC and DEFC.

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Conflicts of Interest: The authors declare no conflict of interest.

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