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A Novel Pt/C Electrocatalyst Impregnated by Phosphomolybdic Acid as CO-tolerant anode catalyst for Proton Exchange Membrane Fuel Cells

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Abstract

Proton exchange membrane fuel cells (PEMFCs) use chemical energy of hydrogen to generate electricity together with water as a by-product. However, the PEMFC performance and durability is significantly deteriorated with hydrogen fuel containing even small amount of CO which is strongly adsorbed on platinum (Pt) catalyst; hence, the number of active sites greatly decreases especially at low reaction temperature. Therefore, this work focuses on the development of a novel Pt-based electrocatalyst to improve catalytic performance at room temperature. Pt-based carbon supported (Pt/C) catalyst impregnated with phosphomolybdic acid ($H_3PMo_{12}O_{40}$ or denoted as PMA) was developed in this work. The effect of PMA content on improving the catalytic activity and CO tolerance was investigated using several diagnostics: scanning electron microscopy, energy dispersive x-ray spectroscopy, transmission electron microscopy and cyclic voltammetry. It was found that the introduction of PMA into Pt/C catalyst had no significant effect on its physical structure. In the CO-stripping experiment, 40 % wt PMA on Pt/C catalyst exhibited a 1.5-fold increase in the peak current in comparison with pure Pt/C. Conversely, the PEMFC performance was found to improve to a certain extent of the PMA content in which the PEMFC containing 20 % wt PMA-Pt/C catalyst provided a maximum power density with an excellent CO tolerance.

Keywords: Proton Exchange Membrane Fuel Cells; Polyoxometalate; CO tolerance; Heteropoly acids

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) have been considered as an ideal energy conversion device for mobile and stationary applications because of their high efficiency, high power density, fast response, low temperature operation, and zero emissions. In PEMFCs, carbon supported platinum (Pt/C) is generally adopted as the electrocatalyst for the

oxygen reduction reaction (ORR) at the cathode and the hydrogen oxidation reaction (HOR) at the anode. However, platinum based electrocatalyst is severely deteriorated with hydrogen gas containing small amount of carbon monoxide as it is commonly produced by steam reforming or partial oxidation of hydrocarbons. In fact, strong Pt-CO adsorption causes a decrease in the

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number of active sites; hence, the cell performance and durability greatly reduce.

Several previous studies have been conducted to improve the CO tolerance of PEMFCs, for instance, development of Pt-based alloys [1-6], modification of electrode configuration [7], utilisation of novel PEMs for high temperature PEMFCs [8-10] and introduction of hetero polyacids such as polyoxometalates (POMs) [11-15]. Among several approaches, the incorporation of phosphomolybdic acid (PMA) to Pt-based electrocatalyst has been extensively studied, owing to their ease of synthesis, great ability for CO electrooxidation, and improvement of durability.

The study of PMA loading on Pt-based electrocatalyst was previously undertaken in order to improve the CO tolerance of PEMFCs; however, the quantity of PMAs has been investigated only up to 16.7 % wt [16]. In this present study, a wide range of PMA loadings (from 0 to 40 % wt) were impregnated on Pt/C catalysts to verify the effect of PMA loading on improving the electrocatalytic activity together with CO tolerance. The different electrode materials were then investigated using several diagnostics: electrochemical techniques, transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Finally, the real application of PMA and Pt/C co-catalyst to PEMFCs was carried out where H₂ or mixed CO-H₂ gas was used as a fuel.

2. Materials and Methods

The 20 % wt Pt/C catalyst utilised as substrates for PMA impregnation, Nafion[®] 117 membrane and the commercial gas diffusion layer (GDL) containing 5 % wt PTFE (Toray H-60) were

purchased from Fuel Cell Store. All other chemicals were purchased from Sigma Aldrich[®].

2.1 Preparation of PMA impregnated on Pt/C electrocatalyst (PMA-Pt/C)

The H₃PMo₁₂O₄₀ impregnated on 20 % wt Pt/C electrocatalyst powder (denoted as PMA-Pt/C) was prepared according to Choi and co-workers [16]. Briefly, a mixture of phosphomolybdic acid hydrates (H₃PMo₁₂O₄₀·xH₂O) and 20 ml distilled water was initially prepared at different concentrations depending on the desired PMA loadings of 10, 20 and 40 % wt in Pt/C catalysts (denoted as 10PMA-Pt/C, 20PMA-Pt/C and 40PMA-Pt/C respectively). Next, the PMA aqueous solution was mixed with Pt/C slurry containing 0.6 g of 20 % wt Pt/C catalyst powder in distilled water and subsequently sonicated at room temperature for 12 hours. The PMA-Pt/C powder was separated using a high-speed centrifuge and then dried in a vacuum oven at 40 °C for 48 hours.

2.2. Characterisation of PMA-Pt/C catalyst

The CO tolerance of various PMA-Pt/C compositions was examined through electrochemical techniques. This work employed CO stripping measurement based on a three-electrode system consisted of a glassy carbon working electrode coated with PMA-Pt/C particle, a Pt rod as a counter electrode, and Ag/AgCl as a reference electrode.

The working electrode was made of a glassy carbon paper coated with a PMA-Pt/C layer by a drop casting method. The PMA-Pt/C catalyst ink was prepared from 5 mg PMA-Pt/C powder, 50 µl Nafion[®] 117 solution and 1 ml of 5 M ethanol solution. A sonication for at least 30 minutes was

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required to ensure a well-mixed suspension of the catalyst ink. Then, 75 μl of the catalyst ink was dropped onto glassy carbon paper and then dried at 60 °C for 1 hour in a vacuum oven. Prior to the CO-stripping measurement, 0.5 M H_2SO_4 electrolyte solution was purged with N_2 gas for 1 hour to remove dissolved oxygen in the solution, followed by CO gas (1000 ppm in N_2 gas) at a flow rate of 200 ml min^{-1} for 15 minutes. Two voltammetry techniques were sequentially employed as follows. Firstly, the CO pre-adsorption was performed at a potential range of 100-300 mV for various adsorption periods (300-1200 seconds). Before starting the second voltammetry technique, N_2 gas was continuously supplied to the electrolyte solution to entirely remove dissolved and physically adsorbed CO on the electrode surface. The CO stripping test was then carried out using cyclic voltammetry, scanning the potential from -0.2 to 1.2 V at a scan rate of 100 mV s^{-1} .

The morphology and topography of PMA-Pt/C containing various PMA contents were investigated using SEM and TEM, respectively. The PMA contents were also verified using energy-dispersive X-ray spectroscopy (EDX).

2.3 Fabrication of PEMFCs

Catalyst ink used in this work was composed of catalyst powder, Nafion[®] ionomer solution (5 % wt), distilled water and glycerol, which was well mixed using a sonicator. Different types of catalytic materials and compositions were directly deposited onto 5x5 cm teflonated GDLs using a conventional brush-painting method. The commercial teflonated Toray H-60 GDLs were employed as the backing of both anode and cathode sides. Among various electrode

compositions, catalyst loading of 1 mg cm^{-2} was exploited in all membrane electrode assemblies (MEAs). Nafion[®] 117 membrane was used as a proton exchange membrane (PEM), which was pre-treated and activated sequentially with 30 % v/v H_2O_2 , 8 % v/v H_2SO_4 and distilled water for 1 hour each at the same treatment temperature of 80 °C (± 2 °C). After that, the pre-conditioning Nafion[®] 117 membrane was dried in a vacuum oven at 35 °C for 1 hour and then kept in a desiccator until used. Five MEAs using different electrode compositions (i.e. Pt/C, 10PMA-Pt/C, 20PMA-Pt/C, 40PMA-Pt/C and Pt-Ru/C) were fabricated using a hydraulic press (LABTECH) at the temperature of 135 °C, under a pressure of 15 bars, for 2.5 minutes. In order to enhance a good attachment between catalyst layer and PEM, the Nafion[®] ionomer solution (5 % wt) was applied on the catalyst layer as a binder and proton conductor.

2.4 Characterisation of PEMFCs

The PEMFC device was comprised of a MEA (with a geometric active surface area of 25 cm^2), gaskets, bipolar plates, a current collector and clamping bolts and nuts. The schematic diagram of cell performance test setup is demonstrated in Fig. 1. The cell performance was investigated at room temperature under non-humidifying conditions. Air zero (purity 21 % ± 1 % O_2 in N_2) and ultra-high purity (99.99 %) hydrogen were supplied to cathode as an oxidant and to anode as a fuel, respectively, at an identical flow rate of 100 ml min^{-1} (verified by an electronic universal gas flowmeter, Agilent Technologies). The cell potential across anode and cathode subjected to

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change in the load was measured using a digital multimeter (Fluke 289).

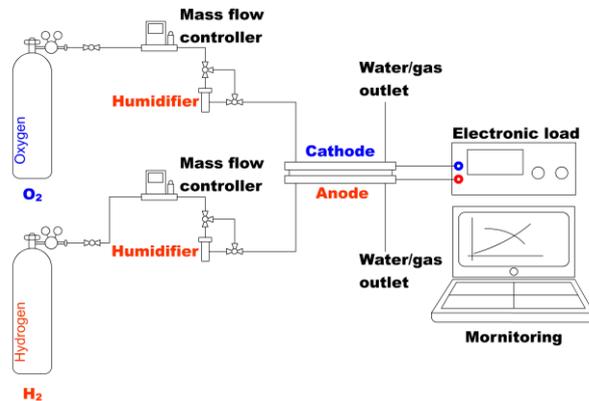


Figure 1 Schematic diagram of cell performance test setup

3. Results and Discussions

3.1 Synthesis of PMA-Pt/C catalyst

Several diagnostics were performed to study the resulting PMA-Pt/C catalyst according to the methodology section. The FTIR spectra of various electrode compositions (shown in Fig. 2) can be used to identify functional groups in different samples. When the PMA was impregnated to the Pt/C catalyst (Fig. 2c), the additional characteristic peaks of the $[PW_{12}O_{40}]^{3-}$ Keggin unit were obtained at 804 cm^{-1} ($W-O_c-W$), 898 cm^{-1} ($W-O_b-W$), 977 cm^{-1} ($W=O_d$) indicating the existence of PMA in the Pt/C catalyst. It was also found that the impregnation of PMA had no adversely effect on the basic structure of Pt/C catalyst as it is intact and preserved when compared Fig. 2b to Fig 2c.

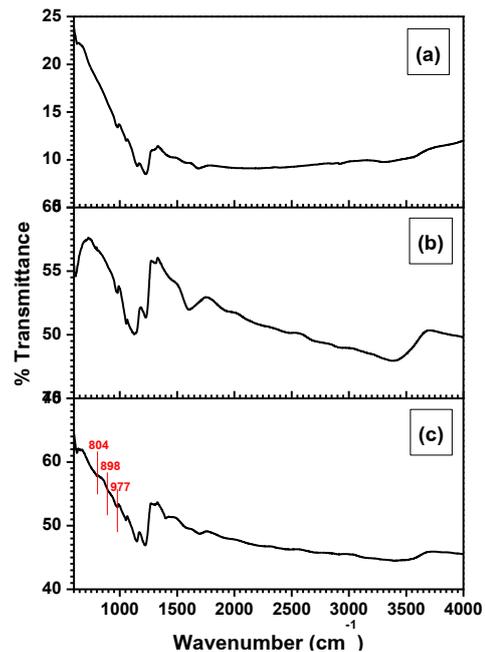


Figure 2 FTIR spectra of (a) Vulcan XC72 carbon black, (b) Pt/C and (C) 20PMA-Pt/C

The microstructural properties of PMA-Pt/C, Pt/C and Vulcan XC72 were investigated using TEM as shown in Fig. 3. All PMA-Pt/C samples contained evenly dispersed Pt nanoparticles with similar particle size in a range of 2-3 nm. This implies that structural properties of Pt were not affected by the presence of PMA which could be supported by the FTIR spectra.

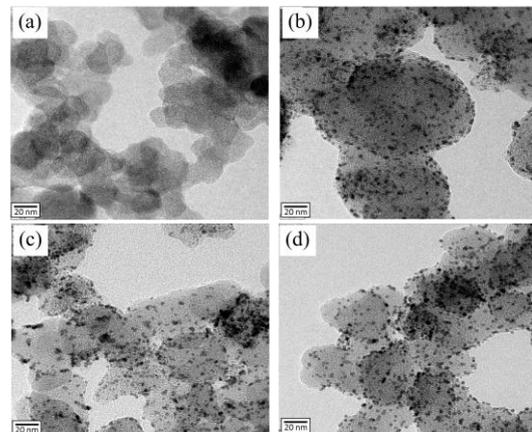


Figure 3 Representative TEM images of (a) Vulcan XC72 carbon black, (b) Pt/C, (c) 20PMA-Pt/C and (d) 40PMA-Pt/C

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The morphology and EDX spectra of PMA-Pt/C containing different PMA quantities are shown in Fig. 4. After being deposited on the Toray H-60 GDL, the similar morphology of PMA-Pt/C agglomerates can be observed in all samples.

The representative EDX spectra reveal their main compositions as detailed in Table 1. The quantity of PMA was determined corresponding to the Mo content. It was found that the percentage of Mo in PMA-Pt/C samples agreed very nearly to the desired Mo loadings despite relatively smaller.

Table 1 The compositions of PMA-Pt/C investigated by EDX

Samples	% concentration (wt)		
	C	Pt	Mo
Pt/C	80.40	19.60	0
10PMA-Pt/C	70.65	21.05	8.30
20PMA-Pt/C	61.06	19.02	19.92
40PMA-Pt/C	44.45	19.87	35.68

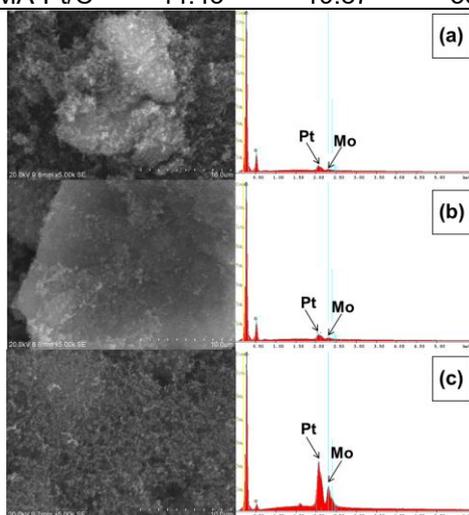


Figure 4 SEM images and EDX spectra of (a) 10PMA-Pt/C, (b) 20PMA-Pt/C and (c) 40PMA-Pt/C

3.2 CO-stripping test of various electrode materials

The CO tolerance of PMA-Pt/C catalysts can be determined by a CO-stripping test using cyclic voltammetry as previously described. All the CO stripping voltammograms shown in Fig. 5 were obtained from the first cycle since they contained the characteristic peaks of CO oxidation. Once the adsorbed CO molecules were completely oxidised from the first potential scan, no CO-stripping peak was obtained in the second-scanned voltammogram (not shown here). In general, the voltammograms of the Pt/C exhibits characteristics of polycrystalline Pt on both the reductive adsorption region of protons and the oxidative desorption region of atomic hydrogen at the potential range of -0.2 to 0.4 V [16]. However, the peak current for hydrogen adsorption on bare surface of Pt was not obtained from the cyclic voltammogram (red line). On the other hand, the presence of PMA in Pt/C catalysts was found to promote the hydrogen desorption and adsorption mechanisms, revealing two dominant characteristic regions. The first region was located in a potential range of -0.1 to 0.4 V which was driven by three different reactions: (i) hydrogen adsorption and desorption on Pt sites, (ii) the reaction of CO molecules on Pt sites, and (iii) the reaction of oxygenated species on Mo sites [17]. These three different reactions occasionally occurred on different Pt and/or Mo sites, resulting in three different oxidative and reductive peaks located in this low potential range. The second peak current was found at around 0.8 V corresponding to the oxidation of pre-adsorbed CO and OH over Pt sites in the PMA-Pt/C catalysts.

When compared among several Pt/C catalysts containing different PMA loadings, it was

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found that an increase in the PMA loading to Pt/C catalysts resulted in the following phenomena: (i) the thickness of electrical double layer greatly expanded further away from the electrode surface which was attributed to a proton transfer redox reaction (O/OH ligands) on the Mo atoms [18], (ii) the CO-oxidation peak current was dramatically improved, and (iii) the second CO-oxidation peak current was transitioned from 0.8 V to the lower voltage of 0.7 V, which can be implied that the pre-adsorbed CO on Pt sites in the PMA-Pt/C catalysts would be easily oxidised when compared to that of the Pt/C catalyst. In addition to the excellent CO-tolerance property of PMA, the 1.5-fold increase in peak current was obtained from 40PMA-Pt/C in comparison with the Pt/C as a result of the existence of Mo co-catalyst.

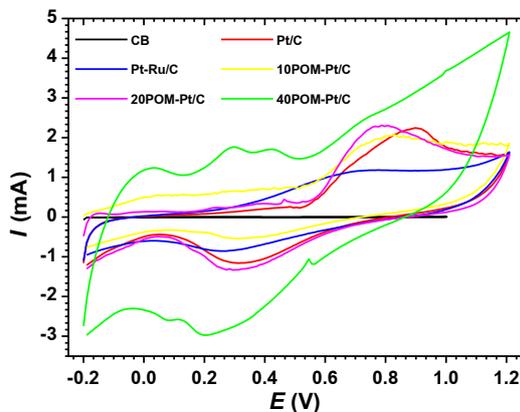


Figure 5 CO stripping voltammograms of various Pt/C catalysts containing different PMA loadings of 0, 10, 20 and 40 % wt (denoted as Pt/C, 10PMA-Pt/C, 20PMA-Pt/C and 40PMA-Pt/C, respectively). The CB and Pt-Ru/C represent Vulcan XC72 carbon black and carbon supported Pt-Ru alloy, respectively.

3.3 The application of PMA-Pt/C in PEMFCs

The application of different anode materials to PEMFCs was investigated using ultra-high purity

(99.99 %) hydrogen and mixed CO-H₂ gas (50 ppm CO) as shown in Fig. 6 and Fig. 7 respectively. In general, it was found that the PEMFC containing 20PMA-Pt/C exhibited the great performance in terms of current generated, power density and CO tolerance when compared with other PMA-Pt/C compositions and Pt-Ru/C. On the other hand, the performance of PEMFC using 40PMA-Pt/C catalyst was relatively low which was contrary to the maximum peak current examined by CO-stripping voltammetry. The extremely high PMA content of 40PMA-Pt/C catalyst limited the passage of hydrogen and oxygen gases to react with highly active Pt catalyst within the PMA-Pt/C to produce water by-product and generate electricity. However, when the mixed CO-H₂ gas was used as a fuel the PEMFCs containing 20PMA-Pt/C and 40PMA-Pt/C revealed a significantly improved CO tolerance with a minimal deterioration of power generated.

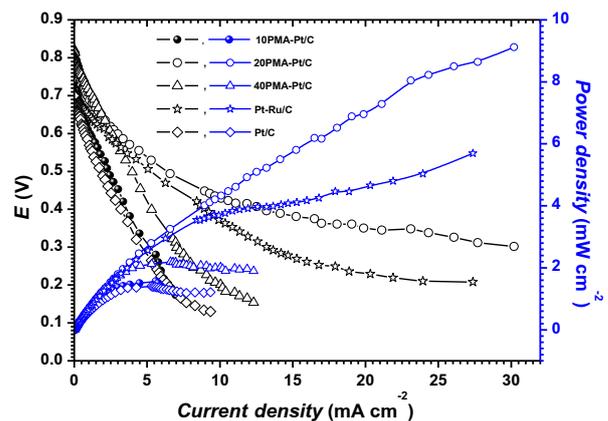


Figure 6 Variation of polarisation and power curves of PEMFCs using different electrode materials on anode including Pt/C, Pt-Ru/C, 10PMA-Pt/C, 20PMA-Pt/C and 40PMA-Pt/C whereas the Pt/C was used as a catalytic material on the cathode for all MEAs. The H₂ and air flow

rate were constantly supplied to the cell at 40 ml min⁻¹.

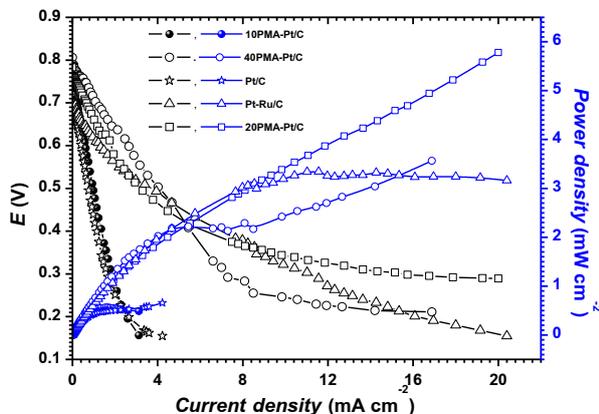


Figure 7 Variation of polarisation and power curves of PEMFCs using different electrode materials on anode including Pt/C, Pt-Ru/C, 10PMA-Pt/C, 20PMA-Pt/C and 40PMA-Pt/C whereas the Pt/C was used as a catalytic material on the cathode for all MEAs. The flow rate of H₂ fuel gas containing 50 ppm CO was applied to the PEMFCs using an identical flow rate of air (oxidant) at 40 ml min⁻¹.

4. Conclusions

The effect of PMA content on improving the catalytic activity and CO tolerance was studied in this work. It was found the impregnation of PMA had no adversely effect on the basic structure of Pt/C catalyst as it is intact and preserved according to the FTIR spectra. This can be supported by the SEM and TEM images which revealed the uniformly dispersed Pt nanoparticles with similar particle size of 2-3 nm in all PMA-Pt/C samples. In order to identify the electrocatalytic activity and CO tolerance of various electrode materials, CO-stripping test was carried out using cyclic voltammetry. When compared among several Pt/C catalysts containing different PMA loadings, it was found that an increase in the PMA loading to Pt/C

catalysts caused an increase in the thickness of electrical double layer, an improved CO-oxidation peak current and a transition from CO-stripping voltage of 0.8 to 0.7 V indicating that the pre-adsorbed CO on Pt sites in the PMA-Pt/C catalysts would be easily oxidised in comparison with the Pt/C catalyst. In addition to the excellent CO-tolerance property of PMA, the 1.5-fold increase in peak current was obtained from 40PMA-Pt/C in comparison with the Pt/C due to the existence of Mo co-catalyst. Among other PMA-Pt/C compositions and Pt-Ru/C, the PEMFC using 20PMA-Pt/C catalyst exhibited the great performance in terms of current generated, power density and CO tolerance.

5. Acknowledgement

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6. References

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