

COMPOSITE OF POLYSTYRENE/ACTIVATED CARBON FROM COAL TAILING/PLATINUM AS AN ELECTRODE CANDIDATE FOR MEMBRANE FUEL CELL

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ABSTRACT

Composite material based on polystyrene-activated carbon/platinum (PS/AC/Pt) has been prepared by variation of weight ratio between polystyrene, activated carbon, and platinum in chloroform solvent. The functional groups of the composite material were identified by FTIR, the morphology and the element composition were analyzed by SEM-EDX, and the proton conductivity was measured by a chemical impedance analyzer. The functional groups of material are similar to polystyrene and indicate no effect on its structure. The surface morphology of the composite membrane is smooth and nonporous. The composite material PS-AC-Pt was successfully made without impurity shown by EDX with carbon and platinum elements. The composite material with the highest Pt content showed the highest proton conductivity at 30°C. The proton conductivity tends to decrease as temperature increases. This composite material can be proposed as a membrane electrode candidate for the fuel cell.

Keywords: Activated Carbon, Composite, Electrode Membrane, Fuel Cell, Platinum, Polystyrene

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INTRODUCTION

The fuel cell is one promising future energy source that can be a solution to overcome the energy crisis. In this cell type fuel reacts with oxygen without burning to produce electricity, water, and heat, so it is environmentally friendly, has no emission gas, and does not cause noise or pollution.¹ The interest in developing fuel cell components forced some research to optimize the membrane as the essential part of the fuel cell.² The most widely used membranes in fuel cells are commercial membranes made from sulfonated fluoropolymers.³ Nafion has high proton conductivity, high hydrophilic stability, and oxidative properties. However, Nafion has a disadvantage: at high temperatures, its conductivity decreases, the price is very high, and the very high methanol permeability value decreases the overall fuel cell performance. Therefore an alternative polymer membrane is needed, such as polymer-based hydrocarbons.⁴ An alternative polymer that can be developed for fuel cell electrolyte membranes is polystyrene in styrofoam waste. Adding these composites will also increase the water absorption capacity of the membrane. Water as a proton (H^+) transport medium is closely related to the proton conductivity of a membrane.^{5,16} The use of carbon has been known to give mechanical reinforcement and outstanding water uptake in the membrane.^{6,7} On another side, carbon from coal tailing is a potential filler material for composite membranes.^{3,8} Addition of carbon in the composite can increase electrical conductivity.⁴ Carbon also increases composite thermal stability.⁹ The existence of platinum (Pt) in an active polystyrene-carbon composite membrane catalyzes both oxygen reduction reaction (ORR) occurring at the cathode and hydrogen oxidation reaction (HOR) at the anode.¹⁰ The central part of fuel cell polarization occurs at the cathode; the hydrogen oxidation reaction becomes much smoother and increases anode activity.^{11,12} This work aimed to evaluate the effect of the composite composition on the physicochemical character and its potency as the electrode in a membrane fuel cell.

EXPERIMENTAL

Materials

Polystyrene was obtained from electronic packing styrofoam waste, coal tailings were taken from the Muara Bangkahulu River, and other chemicals including PtCl_2 , phosphoric acid solution (H_3PO_4), ammonium hydroxide (NH_4OH), chloroform (CHCl_3), and acetone were purchased from Merck Germany.

Preparation of Polystyrene from Styrofoam

Small pieces of Styrofoam samples were soaked in 400 mL acetone for three days to remove impurities. The polystyrene component is isolated from the acetone and heated in the oven at 60°C for 2 hours.

Preparation of Activated Carbon from Coal Tailings

Coal tailing is carbonized in a muffle furnace at 500°C for 2.5 hours. After cooling at room temperature, the obtained carbon is ground and sieved by a $125\ \mu\text{m}$ sieve. Carbon powder was activated by soaking in a 20% phosphoric acid (H_3PO_4) solution overnight. The obtained activated carbon was washed with demineralized water repeatedly until the filtrate was neutral. Activated carbon was heated at a temperature of $100 - 120^\circ\text{C}$ for 2 hours, followed by calcination at 700°C for 2.5 hours. The obtained activated carbon is ground and sifted by a $125\ \mu\text{m}$ sieve.

Synthesis of Membranes

The composite of polystyrene-active carbon/Pt has been prepared by the previous methods.^{8,9} In a 10 mL solution of 25% ammonium hydroxide was dissolved 5 mg PtCl_2 70%. Into this Pt-solution was added 1 g of activated carbon. The mixture was then stirred roughly for 1 hour. One gram of polystyrene and 10 mL CHCl_3 were added together into the mixture. The mixture was stirred further until it became homogeneous. The composite gel was finally printed on a Petri dish of 6 cm in diameter. By the same steps, various composites were prepared by variation of weight ratio of polystyrene: activated carbon: platinum of (1:1:0.005) g, (1:1:0.010) g, (1:1:0.015) g. The samples were denoted as PS/AC/Pt (1:1:0.005), PS/AC/Pt (1:1:0.010) and PS/AC/Pt (1:1:0.015), respectively. As control is used, a composite of PS/AC(1:1).

Characterization

The functional groups of the composite were identified using FTIR Bruker Alpha-P at wave numbers of $4000 - 400\ \text{cm}^{-1}$. The membrane morphology and composite material composition were analyzed using SEM-EDX type JEOL 7001 FESEM. Composite proton conductivity was determined by a chemical impedance analyzer IM 3590. The conductivity was measured in the temperature range of $30-70^\circ\text{C}$.

RESULTS AND DISCUSSION

FTIR Analysis

FTIR analysis was performed to know the functional groups contained in the composite membrane. The results of functional group analysis and absorption bands of infrared wave numbers for each composite membrane composition are shown in Fig.-1. The absorption band that emerges comes from the characteristics of composite compositors or the interaction between polystyrene and activated carbon and Pt catalyst. The spectra of PS-AC composites indicate a shift in absorption wave number (Table-1).

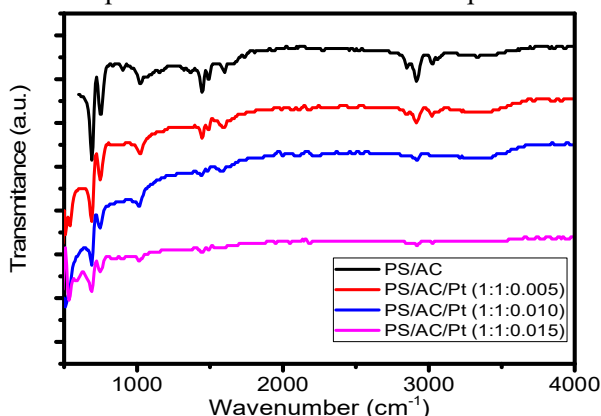


Fig.-1: Infrared Spectra of the Composite Materials

Based on the data in Table-1, which show the type of bond and its wave number and the shifting of several characteristic wave numbers, it is clear that the absorption bands produced are either without or with variations in the relative addition of Pt catalysts. All FTIR spectra do not indicate the existence of a new absorption band for a new functional group from the initial polystyrene constituent. This fact indicates that the addition of activated carbon and Pt catalyst does not affect the structure of the polystyrene component. Both these additive materials serve only as a filler and physical calcification of the composite.

Table-1: Functional Groups of Composite Material

Functional groups	Wavenumber (cm ⁻¹)			
	Composite material			
	00	05	010	015
Stretching vibration C-H aromatic	3020.33	3012.76	3025.68	3025.77
Stretching vibration C-H alkane	2918.12	2918.12	2925.69	2925.69
Stretching vibration C=C aromatic	1597.7-1447.11	1597.77-1447.11	1439.54	1447.11
Stretching vibration C-C	1020.1-902.01	1020,11	1012,54	1020.11
C-H bond on monosubstituted benzene	751.35-688.51	743.78-688.51	743.78-680.18	743.78-690.08

SEM-EDX Analysis

Composite morphology is presented in Fig.-2. Figure-2(a) shows a more delicate and homogeneous morphological surface of PS-AC. There is a tiny pore due to overheating, causing bubbles in the composite. Carbon species are equally distributed; mixing two different compositions seems to have no difference in phase, so this sample is a homogeneous composite. There are very few cavities and pores in activated carbon, with a broad and tight flat section of PS-AC composites that are closed or mixed with polystyrene.¹³ The composite membrane surface is smooth and nonporous. Adding filler into the membrane can form several cavities in the structure. These cavities allow the process of protons to transfer to fuel cells.^{14,17} Otherwise, the PS-AC-Pt composite shows a porous aggregate form (Fig.-2b).

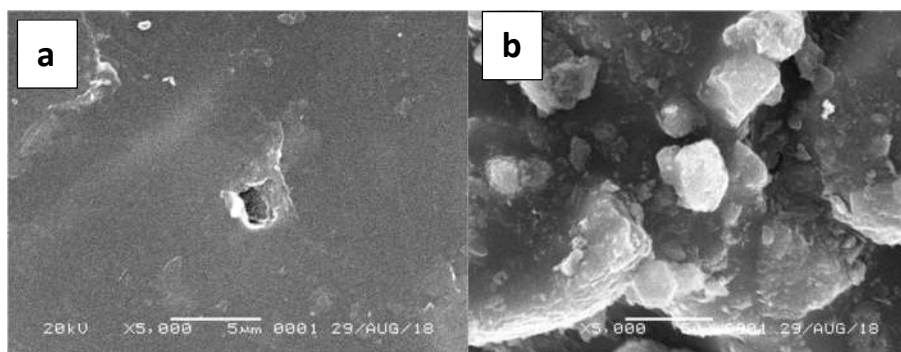


Fig.-2: Micrograph of Composite Material: (a) PS-AC (1:1) g (b) PS-AC-Pt (1:1:0,015)

Compared to the control PS/AC composite, Pt doped composite (PS/AC/Pt) has irregular morphology, tends to be amorphous, and breaks into large clots and splits. These clots and cracks occur due to the unequal distribution of materials and less homogeneous solutions to form a combination in certain parts. Clustering platinum particles occurs in a particular part of the composite. This unequal distribution of platinum particles causes the reaction inside the fuel cell to be not optimal because not all hydrogen gas is facilitated to split into hydrogen ions (H⁺), and consequently, the efficiency of electricity produced is also low.^{15,16} In addition, drying temperature is not suitable for producing a smooth and flat composite surface like PS/AC. The PS-AC composite contains 91.90% carbon and 8.10% Cl (Fig.-3a). There is still a small amount of remained Cl because the drying process does not completely evaporate Cl-precursor. EDX peaks in Fig.-3(b) show carbon and platinum particles that are distributed in the composite. This composite contains 28.99% platinum, 66.26% carbon as the main constituent, and 4.7% oxygen. No other impurities have been identified in the composite.

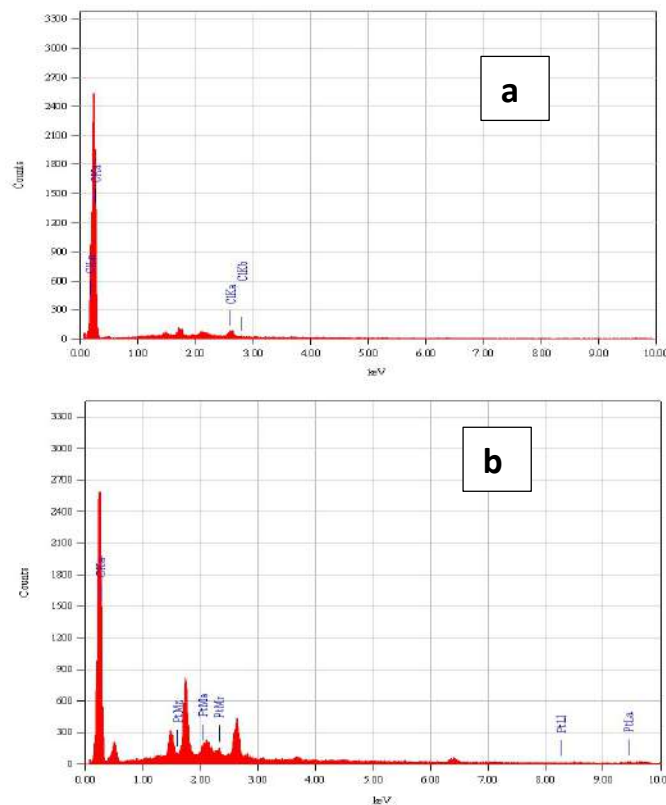


Fig.-3: EDX Analysis of Composite Material (a) PS-AC (1:1) (b) PS/AC/Pt (1:1:0.015)

Proton Conductivity

Figure-4 shows the dependence of the proton conductivity on the temperature. In general, the proton conductivity of composite membranes decreases as temperature increases. This decrease of proton conductivity is associated with the phenomena of relatively low air humidity at high temperature, so that composite material becomes dry condition which causes decreasing proton conductivity.² At high temperatures, the performance of these composites decreases due to the lower water affinity of the composite. The presence of water serves as the main component for facilitating proton conduction. The membrane that can adsorb more water molecules exhibits higher activation energy.² At 30°C the highest proton conductivity of 1.4381×10^{-2} S/cm is achieved by the highest Pt-contained composite. The proton conductivity of composite increases as platinum increases. This fact is attributed to platinum property as good conductive metal. The massive difference in conductivity between metal and non-metal materials is related to the potential difference; in metals, electrons move freely, while in non-metallic materials, it is not so.¹⁵ In addition, at room temperature, the lattice structure of the metal is very regular. The temperature increase affects the lattice structure's irregularity; even higher temperatures can destroy the lattice structure. In this condition, electrons spread and move through the lattice, lowering conductivity. Indeed the conductivity of alloy or metal-containing composite is complex to predict.¹⁶ High thermal treatment of composite material reduces its conductivity.¹⁷ Compared with Nafion-112 which has a chemical impedance of 1.2×10^{-2} S/cm at room temperature, the composite PS-AC-Pt (1: 1: 0.015) g shows higher proton conductivity.¹⁴ The proton conductivity of composites prepared in this work is higher than Nafion at 30 °C. The PS/AC/Pt composite is suitably used at low temperatures. The proton conductivity of the highest Pt-loaded composite sample decreases slightly at 70 °C. A quite lot of platinum content stabilizes the conductivity. Viewed from this matter, this type of composite is capable of being used at high temperature if the platinum content is high enough and equally distributed throughout the structure of the composite, so it does not damage the lattice system and inhibit the movement of electrons. Based on the description above, the PS/AC/Pt composite can be proposed as a candidate electrode for the membrane fuel cell.

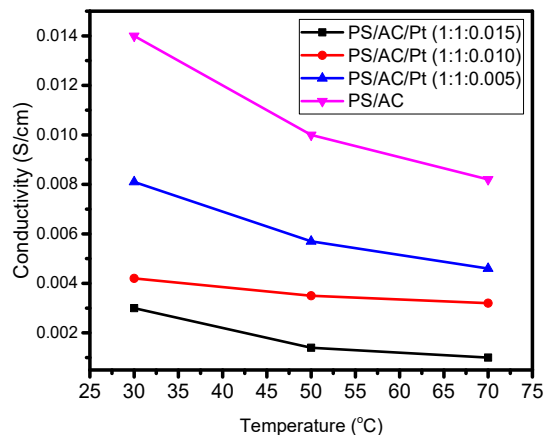


Fig.-4: Dependence of the Proton Conductivity on the Temperature

CONCLUSION

The polystyrene-activated carbon-platin porous composite material was made from styrofoam packing and coal tailing wastes. The addition of activated carbon and Pt catalyst does not affect the polystyrene-based composite structure. The identified functional groups in the composites are similar to polystyrene precursors. The more homogeneous the mixture of precursors, the better the resulting composite. The composite proton conductivity increases as the platinum percentage increases. An increase in temperature decreases the proton conductivity of the composite membrane. The membrane composite prepared in this work showed slightly higher conductivity compared to Nafion. The polystyrene-activated carbon-platinum composite can be proposed as an electrode candidate for the membrane fuel cell.

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