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The enhanced polymer-coated graphite anode electrodes for the electrooxidation of glucose

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ABSTRACT

In this study, poly(N-Isopropylacrylamide) (PNIPAM), poly(acrylamide) (PAAM), poly(acrylic acid) (PAAc), and poly(methacrylic acid) (PMAc) polymers are synthesized by radical polymerization method. The chemical composition and surface morphology of the PMAc polymer are examined by micro-Raman spectroscopy and scanning electron microscopy (SEM). The electrochemical measurements are examined by cyclic voltammetry (CV), chronoamperometry (CA), and electrochemical impedance spectroscopy (EIS) analyses for glucose (Glu) electrooxidation. The characterization analyses reveal that the polymer structure was formed. The electrochemical analysis results indicate that the PMAc/G electrode has higher catalytic activity, stability, and resistance compared to other electrodes with a specific activity of 1.7 mA/cm^2.

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1. Introduction

Fuel cells are an alternative energy source that converts chemical energy into electrical energy, using clean, efficient, cheap, and low CO_2 emissions fuels [1, 2]. Recently, it is an energy source that has been the focus of attention of researchers in response to the problem of environmental pollution and increasing energy demand [3, 4]. Direct fuel cells using fuels such as formic acid [5, 6], methanol [7, 8], ethanol [9, 10], and glucose [11-13] are recognized as emerging power sources for electric vehicles and portable electronic devices. Glucose has recently attracted great interest in fuel cells, which are an alternative energy source, due to the high energy it contains. Glucose is an abundant monosaccharide in nature. Glucose oxidation has been realized as an electrochemical sensor for the control and rapid diagnosis of initial diabetes [14, 15]. Researchers have shown that when glucose is fed into direct fuel cells, it produces 24 electrons. However, it is difficult to break and oxidize since glucose has a very stable molecule. Therefore, it is mostly obtained gluconic acid and 2 electrons according to research [16].

Anode:

$C_6H_{12}O_6 + 2OH^- \longrightarrow C_6H_{12}O_7$ (gluconic acid) $+ H_2O + 2e^-$

Cathode:

$½O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Overall:

$C_6H_{12}O_6 + ½O_2 \longrightarrow C_6H_{12}O_7 + 12H_2O$

Materials such as carbon nanotube, graphene, graphite, carbon black, and carbon fibers have been used as carbon support for fuel cell systems [17-21]. The disadvantages of carbon support materials such as lower interaction and wear prevent parameters such as catalytic activity and durability [22]. Conducting polymers such as polyaniline, polypyrrole, poly(3,4-ethylene dioxythiophene), and poly-3-methyl thiophene have been utilized for fuel cell systems in literature studies [23-26]. Conductive polymers are promising materials as catalyst support or catalyst with advantages such as easy production, chemical stability, high electrical conductivity, and low cost [27]. Inamuddin and Kashmery [28] reported that they developed a graphene@polyanalin-TiO_2 composite for glucose biofuel cell anode applications. They found the current density of this composite by cyclic voltammetry analysis for glucose oxidation with glucose concentrations and glucose oxidase enzyme. Perveen et al [29] reported that they formed a composite material with polypropylene, which is a conductive polymer, iron oxide (Fe_3O_4), carbon nanotube (CNT), and Au, and immobilized it with ferritin and glucose oxidase and embedded it as a bioanode for glucose biofuel battery applications. Haque et al [30] investigated the activity of chitosan@reduced graphene-polyaniline composite

immobilized with ferritin/glucose oxidase enzyme for glucose oxidation by electrochemical analysis.

Table 1. *Summary of literature on electrocatalytic performances for Glu electrooxidation.*

Catalysts	Preperation Method	Specific Activity (mA/cm^2)	Ref.
PdIn/CNT	$NaBH_4$ reduction	0.97	[31]
Au-GtO	Electrodeposition	0.44	[32]
Pd/C	Water-in-oil microemulsion	0.92	[33]
Au@CF	One-pot route	2.00	[34]
Pd-N doped-G/ITO electrode	CVD and Electrodeposition	2.00	[35]

Herein, PNIPAM, PAAM, PAAc, and PMAc polymers were synthesized by the radical polymerization method for Glu electrooxidation. PMAc polymer was characterized by SEM and micro-Raman analysis. Furthermore, the activities, stability, and resistance of polymers were investigated by electrochemical analyses such as CV, CA, and EIS.

2. Experimental

2.1 Synthesis and Characterization

The radical polymerization method was used for the synthesis of polymers. The synthesis of polymers was carried out using N-Isopropylacrylamide, acrylamide, acrylic acid, and methacrylic acid as the monomer, methylene bisacrylamide as a crosslinker, N,N,N',N'-tetramethyl ethylenediamine as an accelerator, and ammonium persulfate as initiator. The distilled water, monomer, crosslinker, and accelerator materials were added and mixed into a vial, except for the initiator ammonium persulfate. Finally, the initiator was added and, after mixing, it was transferred to coat the graphite (G) which is the pencil tip. Thence, G pencil tip electrodes coated with polymer were obtained. SEM analysis was obtained with a Zeiss Sigma 300 instrument to examine the surface morphology of the polymer. Micro-Raman (WITech alpha 300R) analysis was applied to examine the bonds formed by atoms or molecules formed in the structure of the polymer.

2.2 Electrochemical Analysis

Electrochemical analyzes were performed with CV, CA, and EIS measurements using a CHI660-E potentiostat. This system was a three-electrode system such as a working electrode (polymer/graphite), reference electrode (Ag/AgCl), and counter electrode (Pt wire). All analyses were realized in 1 M KOH + 0.5 M Glu solution at room temperature. CV analyses were performed at a scan rate of 100 mV/s in the potential range of -0.65 ~ 0.65 V in 1 M KOH and 1 M KOH + 0.5 M Glu solutions. CA curves for the stability of polymers were performed at 0.6 V potentials during 1000 s in 1 M KOH + 0.5 M Glu. The electrochemical resistance of polymer/G electrodes was examined by EIS at 316 kHz-0.046 Hz frequency and 5 mV amplitude.

3. Results and Discussion

3.1 Physical Characterization

SEM analysis was obtained to examine the surface structure of the obtained polymer. Figure 1 shows SEM images of PMAc. As can be seen from Figure 1, it was observed that PMAc polymer structures were formed. Micro-Raman analysis was performed to examine the molecular structure of the polymer. The Raman spectrum of the PMAc polymer was given in Figure 2. Three main Raman peaks (D, G, and 2D) occur in Raman spectroscopy for PMAc polymer. The D band shows the irregularity in the carbon structure, while the G band reveals the relative graphitization degree [36]. Raman peaks at 1450 cm^{-1}, 1695 cm^{-1}, and 2939 cm^{-1} correspond to the D, G, and 2D bands, respectively. The I_D/I_G ratio was used to measure the disorder in the structure. The calculated I_D/I_G ratio for PMAc polymer was found to be 1.1. If the I_D/I_G ratio was greater than 1, it means that the polymer structure was disordered.

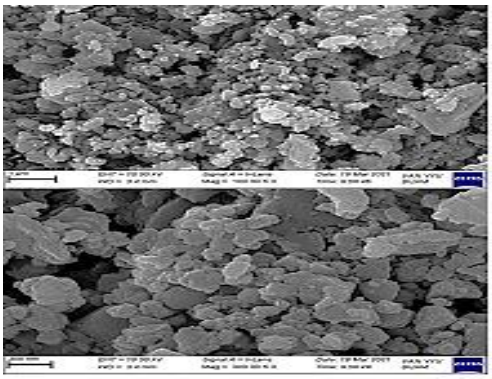

Figure 1. *SEM images of PMAc.*

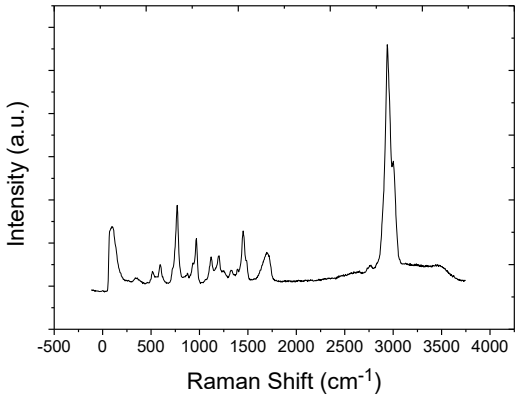

Figure 2. *Micro-Raman spectrum of PMAc*

3.2 Electrochemical Results

CA, CV, and EIS measurements were realized to investigate the electrochemical performance of the polymers. The catalytic activities of the polymers against Glu electrooxidation were determined by CV analyses. CV analyses of polymer electrodes were given in Figure 3(a, b). Although it contains high energy in its glucose structure, the current density was evaluated over the total current in the CV analysis, since it is difficult to decompose. The current densities of the G, PNIPAM/G, PMAc/G, PAAM/G, and PAAc/G polymer electrodes are 0.6 mA/cm^2, 1.6 mA/cm^2, 1.7 mA/cm^2, 0.5 mA/cm^2, and 0.9 mA/cm^2, respectively. The PMAc/G electrode exhibited the best catalytic activity compared to the others. In addition, when comparing two different solutions of 1 M KOH (1.2 mA/cm^2) and 1 M KOH + 0.5 M Glu (1.7 mA/cm^2) for PMAc/G electrode, the difference between them is due to fuel (glucose).

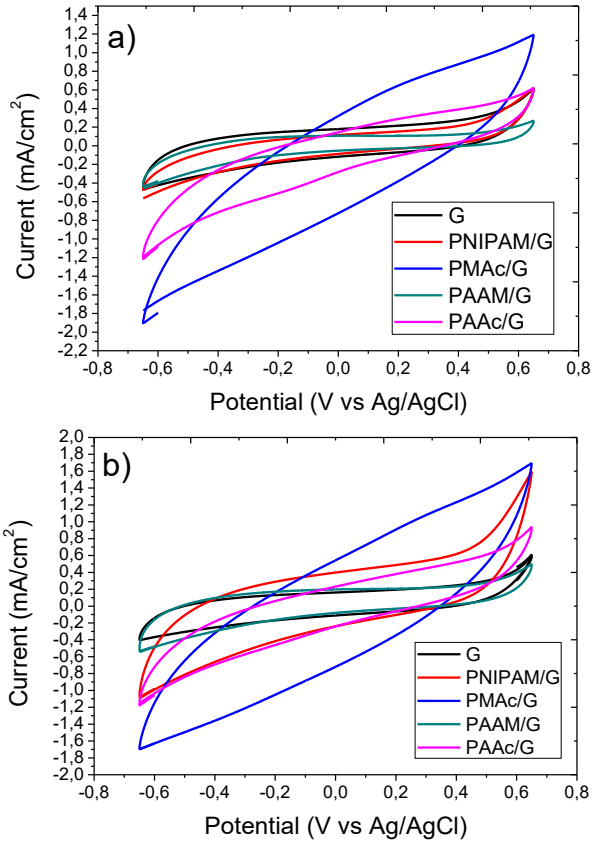

Figure 3. *CV analyses of (a) 1 M KOH and (b) 1 M KOH + 0.5 M Glu for polymer/G electrodes at a scan rate of 100 mV/s.*

CA and EIS analyses were performed to measure the stability and resistance of the polymer electrodes. Figures 4a and b illustrate the stability of the polymer electrodes for 1000 s at a potential of 0.6 V. The PMAc/G electrode was more active and stable than the other electrodes with a specific activity of 0.16 mA/cm^2 obtained after 1000 s. Figure 4c shows the Nyquist plots obtained from the EIS analysis at 0.6 V potential to examine the electrochemical resistance of the polymer electrodes. As the diameter of these plots decreases, the electrochemical resistance increases. PMAc electrode had the best electrochemical resistance as it had the lowest diameter compared to the others.

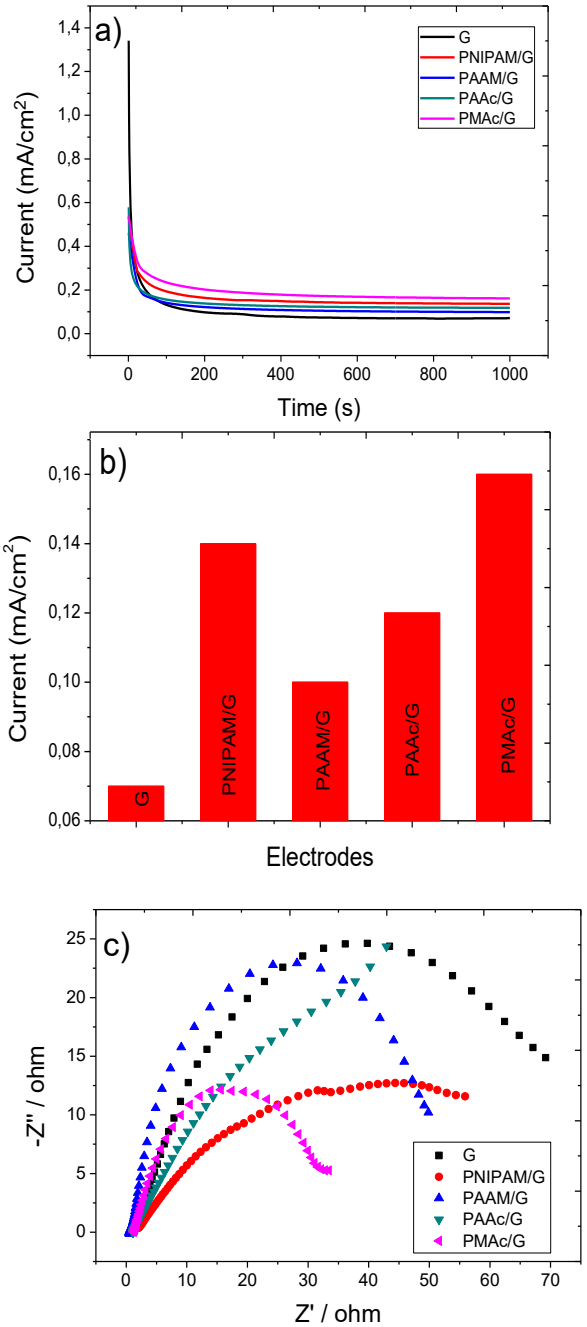

Figure 4. *(a) CA curves of polymer/G electrodes at 0.6 V potential, (b) specific activities after 1000 s, and (c) Nyquist plots of polymer/G electrodes at 0.6 V potential in 1 M KOH + 0.5 M Glu.*

4. Conclusion

The radical polymerization method was used for the synthesis of polymer electrodes. The activity, stability, and resistance of G, PNIPAM/G, PMAc/G, PAAM/G, and PAAc/G electrodes against Glu electrooxidation were investigated by CV, CA, and EIS analyses, respectively. Furthermore, the physical structure and morphology of the PMAc electrode were characterized by SEM and micro-Raman spectrum analyses. The characterization results showed that the polymer structure was formed. The PMAc electrode exhibited the best catalytic activity compared to other electrodes, with a specific activity of 1.7 mA/cm^2. In addition, it was observed that it had the best stability and resistance as a result of the CA and EIS analyses as in the CV analysis.

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