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Research Paper

Modification of Pt-Porous Composite Material (Pt-PCM) and Its Application for Electroanalysis of Uric Acid and Electrosynthesis of Acetic Acid from Ethanol

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Abstract
Research on the synthesis of Pt-Porous Composite Material (Pt-PCM) has been done. This material is used for the electrochemical activity of uric acid and electrochemical synthesis of acetic acid from ethanol. Pt-PCM is made by mixing 99.995% platinum powder and PVC or Poly (vinyl chloride) homogeneously with a homogenizer for 3.0 h, plus tetrahydrofuran solvent, and pressed with a strength of 10 tons/cm^2. The material produced was analysis using Scanning Electron Microscopy (SEM), voltammetry potential V and Tafel plot. The material is used as an electrode for the determination of uric acid and the synthesis of acetic acid from ethanol. The results showed that Pt-PCM has evenly distributed pores and has a perfect Tafel slope compared to metal platinum or solid platinum. Pt-PCM also has the excellent ability as a working electrode for the analysis of uric acid in human urine and electro synthetic acetic acid from alcohol. In conclusion, Pt-Porous Composite Material (Pt-PCM) is a porous material, so it is excellent as a candidate for electrodes.

Keywords
Platinum, Composite, Porous, Uric Acid, Acetic Acid

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1. INTRODUCTION

Platinum is a metal that has high stability against temperature, resistant to corrosion and good electrical conductors. This metal has been named a precious metal. This metal is more tenacious than copper, silver, or gold, so it is the strongest metal compared to other metals, but harder than gold. This metal is used as a catalyst in a variety of environmentally friendly energy processes, including as a catalyst converter and fuel cell. This valuable metal is used in chemical reactions for various products and processes, such as converting toxic carbon monoxide to less dangerous carbon dioxide through a catalytic converter process. Thanks to the superiority of platinum catalysts that can produce safer products, many industries in the world use platinum as a catalyst in their industrial processes.

Platinum is used as an electrocatalyst for the electrochemical oxidation process (Chen and Schell, 2000; Tripković et al., 2001; Iwasita, 2002). Solid platinum has several disadvantages, namely a small surface area and a high price. Porous platinum electrodes have a high activity widely used in batteries, fuel cells, and sensors because they have high efficiency and are used for a variety of products with small sizes. Platinum has the modification of platinum in the form of porous platinum. Porous platinum has a large surface area, so it contacts more target compounds (Boretius et al., 2011). Therefore, in this paper, the results of the study are modified porous platinum or known as Pt-Porous Composite Material (Pt-PCM). The Pt-porous composite material that has been made is applied as a working electrode for uric acid analysis and as an anode for the production of acetic acid from ethanol.

The stability and reactivity of porous platinum metal has a very good response to the detection of uric acid by electroanalytic techniques. Purine metabolism in the human body produces uric acid which is excreted in the urine. Uric acid in urine and serum has a long residence time. Uric acid in the urine can be sampled to help diagnose various diseases such as hyperuricemia, gout and Lesch-Nyhan syndrome. Various studies of modification of platinum metal to detect uric acid in urine and blood (Sadikoglu et al., 2011). Spectrophotometric methods are often used in the biomedical field to determine uric acid concentrations in urine and blood. The reagents used were phosphotungstic acid and uricase enzymes (Chen et al., 2005). Electrochemical methods are often used to detect uric acid using modified carbon electrodes. The method that is of-

Table 1. Electrosynthesis Results in 0.25 M Ethanol in 1.0 M KOH with a Potential of 1.05 V and an Electrolysis Time of 6 Hours

Electrodes	Acetic Acid (%)	Current Density (mA/cm^2)	Current Efficiency (%)	Power (kWh/ton)
Pt-solid	15.00	44.30	48.33	5657.53
Pt-PCM (Porous)	53.21	462.29	24.45	15231.72

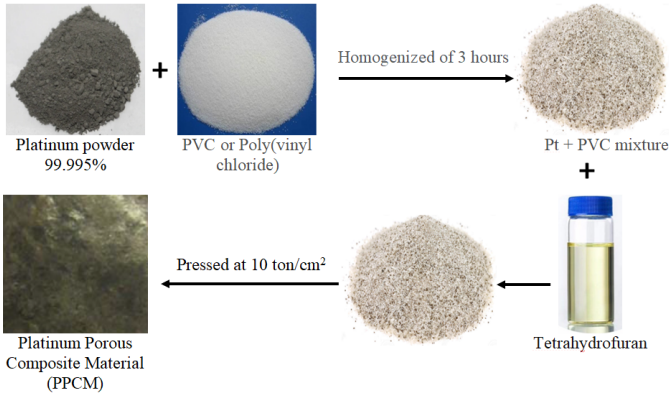

Figure 1. The Schematic for the Preparation of the Pt-Porous Composite Material (Pt-PCM)

ten used is voltammetry using screen-printed carbon electrodes (Reanpang et al., 2021), Au-Pd electrodes (Matos et al., 2000), GC-propionyl choline (Lin and Jin, 2005), graphite-DNA (Luo et al., 2005), GC-norepinephrine (Zare et al., 2005), GC-5-hydroxytryptophan (Lin and Li, 2006), carbonation paste (Shahrokhian and Ghalkhani, 2006), and GC-CeO_2 (Wei et al., 2006). The effect of variations in concentration on uric acid analysis using the cyclic voltammetry method with a modified GCE electrode (Sadikoglu et al., 2011).

Platinum has used various electrochemical oxidation. The electrochemical oxidation of methanol using Pt electrodes with metal catalysts and carbon supports (Xu et al., 2004). Solid Pt electrodes are used to produce formaldehyde from methanol (Childers et al., 1999). The polymers can be used as beneficial support because the spread of metals is more homogeneous to prevent grouping (Arias et al., 2004). The PVC has been used as a metal binder for the preparation of composite material (Pereira et al., 2004). Pore structure and large surface area if the manufacture of electrodes using polymer support with porous platinum. This electrode modification aims to increase the sensitivity and selectivity in uric acid analysis.

The purpose of this research is the preparation of porous platinum material with the name Pt-Porous Composite Material (Pt-PCM). Pt-PCM has properties of high porosity, high surface area, durability, and excellent electrocatalyst. Pt-PCM is prepared using a simple method and unique material for electroanalysis and electrosynthesis.

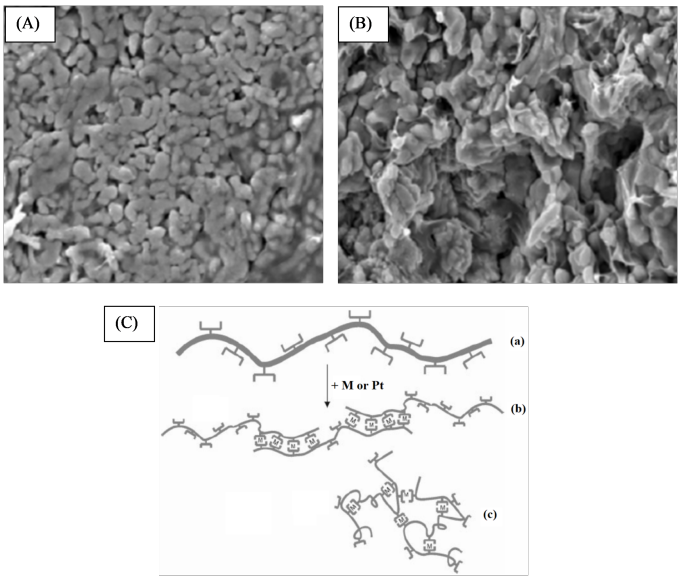

Figure 2. SEM Image of (A) Pt-PCM Surface (B) Pt-PCM Cross-section and (C) Bonding Metal with PVC, with a Magnification of 1000×

2. EXPERIMENTAL SECTION

2.1 Materials and Instrumentation

Platinum powder, Polyvinyl chloride (PVC), Tetrahydrofuran (THF), uric acid, NaOH, KOH, KCl, and NaCl were used in this research from Merck (Germany). PGSTAT 100 N/250 mV from Metrohm Autolab was used for the electrochemical studies. Pt wire, Pt-PCM, and Ag/AgCl were used as the counter, working, and reference electrode.

2.2 Preparation of Pt-PCM Material

Porous platinum electrodes are prepared according to Figure 1. Porous platinum is prepared by mixing the platinum powder with grain size 0.5-1.2 micron with PVC (polyvinyl chloride) until homogeneous for 3 h. A homogeneous mixture was added with tetrahydrofuran, then pressed at a pressure of 10 tons/cm^2. Porous platinum solids were analyzed using SEM for working electrodes and anodes.

2.3 Application of Pt-Porous Composite Material (Pt-PCM) for Uric Acid Analysis

The Pt-PCM prepared was designed as a working electrode. Uric acid was analyzed using cyclic voltammetry method. Uric acid analysis in electrolysis cells using Pt-PCM, solid platinum, and Ag/AgCl electrode. Cyclic voltammetry analysis of uric

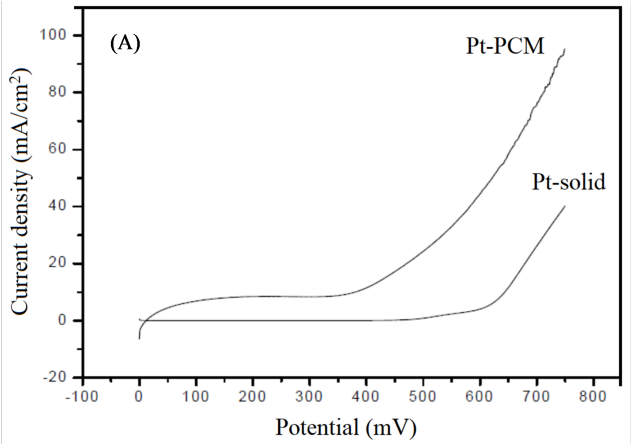

Figure 3. Voltammogram Potential Linear (A) and Tafel Plot (B) Using Pt-solid and Pt-PCM in 0.25 M Ethanol Using 1.0 M KOH, with Scan Rate 1.0 mV/s

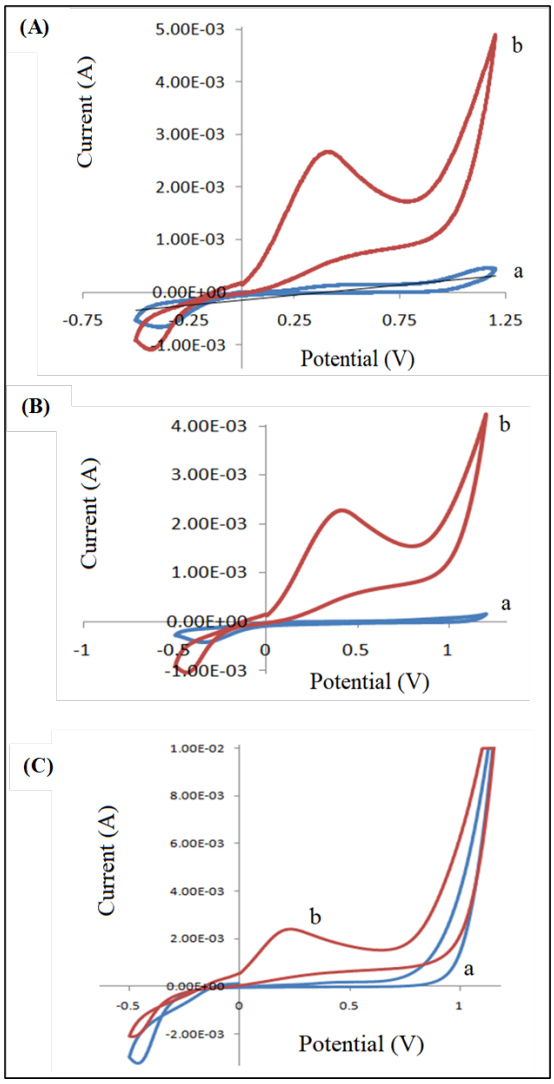

Figure 4. Voltammogram Cyclic of the Pt-PCM in 0.003 M Uric Acid (A) 0.1 N KCl (B) 0.1 N NaCl dan (C) 0.1 N NaOH. (a) Electrolyte without Uric Acid and (b) Electrolyte + Uric Acid Using Scan Rate 100 mVs^{-1}

acid was performed in 5 mL NaOH 0.1 M, 0.015 M uric acid, and 5 mL urine samples.

2.4 Application of Pt-Porous Composite Material (Pt-PCM) for Electrosynthesis Acetic Acid from Ethanol

Pt-PCM is used as an anode and metal platinum as a cathode for electrosynthesis acetic acid from ethanol. Electrolysis of 0.25 M ethanol using 1.0 M KOH as electrolyte for 6.0 h with a fixed of 1.05 V. Electrosynthesis results was analyzed using HPLC.

3. RESULTS AND DISCUSSION

3.1 Pt-Porous Composite Material (Pt-PCM) Characterization

Figure 2 shown the results of Pt-PCM material characterization with SEM. Figure 2a shows the Pt-PCM surface of a porous material. Pt-PCM has a porous surface, a non-smooth surface. Figure 2b. shows of Pt-Porous Composite Material (Pt-PCM) in the cross-section. The Pt-PCM results from the preparation show a porous surface. This porous surface is an excess of Pt-PCM material. Porous surfaces provide benefits to the material because the surface area will be even higher. Figure 2c shows the role of PVC in binding platinum. Platinum will be firmly bound in PVC so that it does not dissolve easily (Meier and Schubert, 2003).

Besides characterization with SEM, Pt-PCM electrodes are characterized using linear potential V and Tafel plot, as shown in Figure 3. Figure 3a shows that Pt-PCM material has a higher electrochemical response compared to solid platinum. The Tafel plot in Figure 3b was showing that the Pt-PCM has a higher Tafel plot value compared to the Pt metal. The quality of Pt-PCM material was evaluated using linear potential parameters and Tafel plots (Shen and Xu, 2006; Tarasevich et al.,

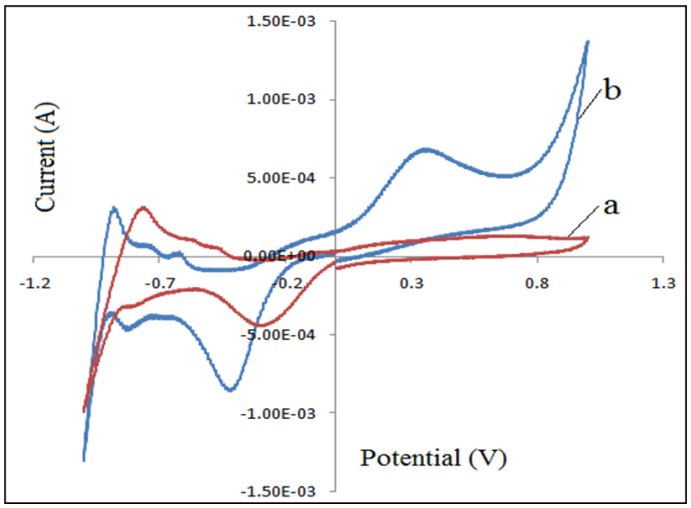

Figure 5. Voltammogram Cyclic of the Pt-PCM in Uric Acid 0.003 M + 0.1 N KCl at Potential Area -1.0 up to +1.0 V using scan rate 100 mVs^{-1}

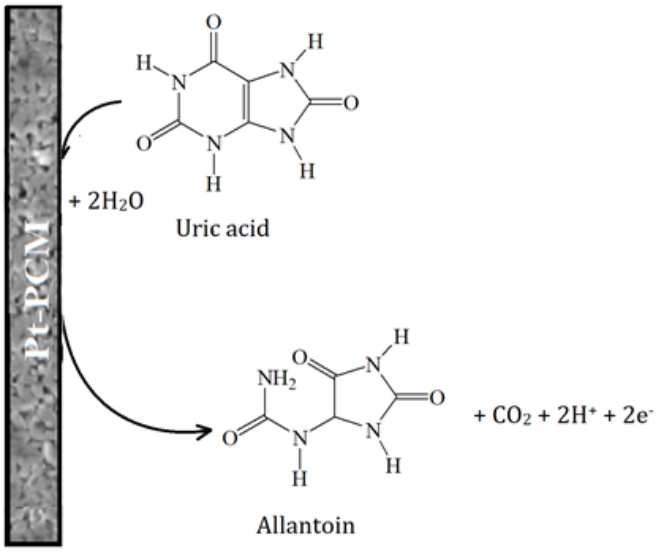

Figure 6. The Electro-oxidation of Uric Acid to Allantoin Using Pt-PCM Electrode

2005; Xu et al., 2005). The preparation of porous electrodes made by combining powder platinum with PVC adhesives has resulted in a material that has excellent quality. Besides having high pores, the material exhibits excellent electrocatalytic performance based on Tafel plot values for Pt solid 188 mV/dec, and Pt-PCM material has Tafel plots of 468 mV/dec.

3.2 Application of Pt-PCM for Electroanalysis of Uric Acid

The electrochemical activity of Pt-PCM was carried out using cyclic voltammetry of uric acid with various types of electrolytes. Platinum is very reactive in strong acids, such strong acids like concentrated HCl and H_2SO_4 used as electrolytes. Cyclic voltammetry of uric acid was carried out using salt electrolytes such as KCl, NaCl, and NaOH. Figure 4a and 4b show a uric acid voltammogram with Pt-PCM electrodes in the KCl and NaCl electrodes. The two electrolytes produce voltammograms that are almost identical. Uric acid oxidizes at a potential of 0.35 V to form allantoin.

Platinum is an inert metal, so it is not reactive to salt electrolytes. The oxidation peak on the cyclic voltammogram shows the oxidation of uric acid. The peak on a negative blood scan shows that uric acid has not been reduced. Both KCl and NaCl electrolytes showed good ability in the uric acid analysis. KCl is a better electrolyte than NaCl because it provides greater current. NaOH electrolytes give very satisfying results for the oxidation of uric acid (Figure 4c).

Figure 5 shows voltammogram cyclic using the potential area of -1.0 to 1.0 using KCl electrolytes. With a negative potential, several peaks are associated with platinum activity in KCl. Although platinum is inert, platinum has an excellent ability to adsorb H^+ ions from water. The addition of uric acid in Figure 6b causes an increase in peaks in unfavorable areas. The addition of uric acid causes acid concentration to increase so that it experiences a peak increase. Figure 6 shown of the electrochemical oxidation of uric acid on Pt-PCM electrode (Khan et al., 2013; Wang, 2011).

Figure 7 shows the cyclic voltammograms using Pt-PCM electrodes for uric acid analysis. Figure 7a shows a voltammogram with a concentration of uric acid 0.001-0.005 M. Figure 7b shows a voltammogram with a uric acid concentration of 0.005-0.025 M. A low uric acid concentration (0.001-0.005 M) produces a calibration curve with R^2 of 0.679, while with a uric acid height concentration (0.005-0.025 M) provides a calibration curve with R^2 of 0.993. The results of the validation of the uric acid analysis test method with Pt-PCM electrodes showed LOD is 0.67 mM and LOQ is 2.24 mM,, with 4.73% precision and recovery of 100.26%.

3.3 Application of Pt-PCM for Electroorganic Synthesis of Acetic

Preparation of Pt-PCM applied for convertion of ethanol to acetic acid. Electrosynthesis is different from electroanalysis. This study was using a two-electrode system the anode, and cathode. Pt-PCM is used as an anode and solid platinum is used as a cathode. Ethanol with a concentration of 0.25 M added with 1.0 M KOH electrolyte using a fixed potential of 1.05 V and electrolysis time for 6 hours obtained the data in Table 1.

Figure 8 shows the electrooxidation mechanism of alcohol to acetic acid. Platinum acts as a place of oxidation and electrocatalyst. Ethanol in alkaline solution is oxidized on the Pt surface at potential of 0.35 V (Christensen et al., 2013). This potential difference is caused by the electrolyte concentration and the scan speed used differently. The primary alcohol oxidation reaction on the surface of the platinum electrode in alkaline solution follows the mechanism of Figure 8 (Chen and

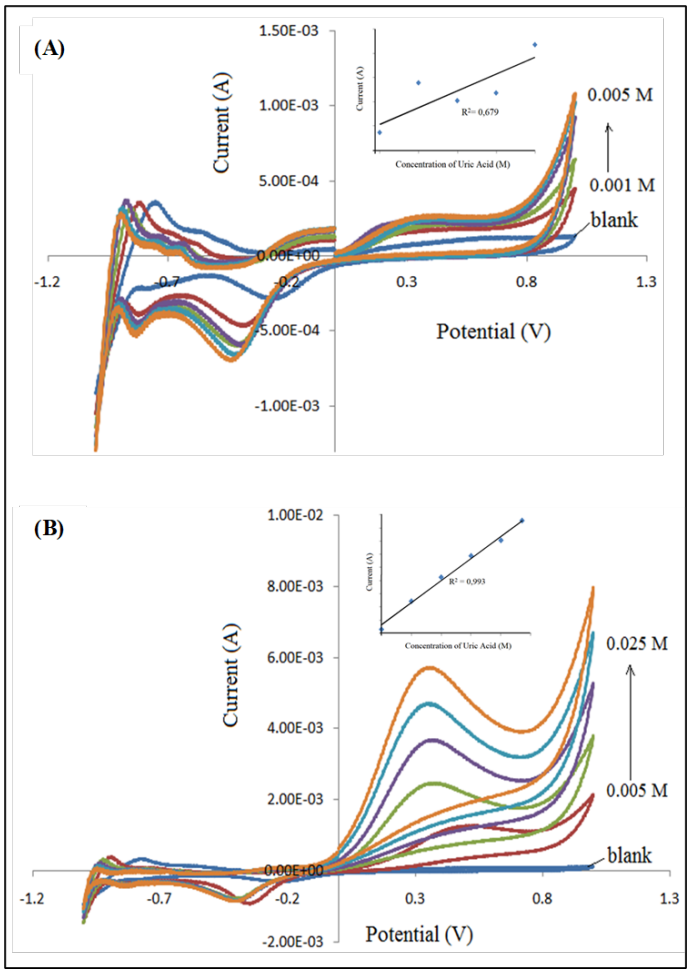

Figure 7. Voltamograms Cyclic Using Pt-PCM Electrode in NaOH 0.1 M 5 mL: (A) Uric Acid 0.001-0,005 M 20 mL (B) Uric Acid 0.005-0,025 M 20 mL with Scan Rate 0.1 Vs^{-1}

Schell, 2000). The results of their research showed that at a potential of 0.8 V, ethanol oxidation occurred on the surface of platinum metal in alkaline solution. The Pt metal is a good material for absorbing organic molecules and breaking intermolecular bonds (Iwasita, 2002). The saturated alcohol can interact with catalyst metals when oxidized (Christensen et al., 2013). Ethanol can be through two reactive sites during the adsorption process, namely OH groups or carbon atoms as conveyed in the following reactions.

Ethanol is adsorbed on the platinum surface to form two products Pt–OCH_2–CH_3 and Pt–CHOH–CH_3 by releasing H^+ and electrons. Pt metal activity in alkaline solution occurs adsorption of OH ions to form Pt-OH and the further process forms Pt-O (Tripković et al., 2001). The complete reaction for ethanol oxidation on Pt electrodes is oxidized to become aldehydes (R-COH) and reacts further to form carboxylic acids (R-COOH). Reactive intermediates (R-COads) are produced through alcohol. Then react with the OHads species of OH– that are absorbed to form acids. The final product of the oxidation of ethanol in alkaline solution is the R-COO- anion. The mechanism of ethanol oxidation reaction that occurs between solid platinum and Pt-PCM is the same, but Pt-PCM electrode have high surface area, so it is more effective.

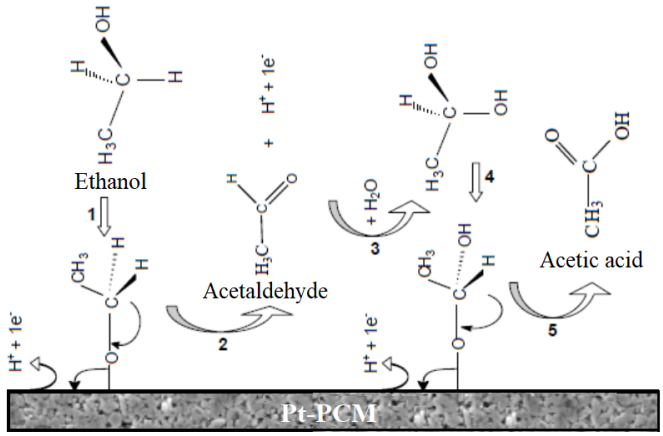

Figure 8. Mechanism of the Electrosynthesis of Acetic Acid on Pt or Pt-PCM Electrode Surface

4. CONCLUSION

Pt-Porous Composite Material (Pt-PCM) results of the preparation have shown excellent character that is a porous material that has a high current density and Tafel plot compared to platinum in metal form. Pt-PCM electrode showed excellent performance for the electroanalysis and electrosynthesis of uric acid and acetic acid, respectively. Pt-PCM is an alternative material for obtaining materials with high surface area, durability, and suitable electrocatalyst.

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