Synthesis of PANi-TiO$_2$ composite and preparation of Ti/PANi-TiO$_2$ electrode for electrochemical study in brewery wastewater

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Abstract

PANi-TiO$_2$ composites are successfully synthesized by chemical method using TiO$_2$ from 30 to 80 wt% to aniline during polymerization process for improving their material properties. Their conductivity was characterized by I-E curves among them the highest one (13.37 mS/cm) reached by using 40 wt% TiO$_2$. Their paste form was made by using chitosan acetic acid solution as binder agent for preparing Ti/PANi-TiO$_2$ electrode which measured in brewery wastewater by electrochemical impedance. It was found an electrical equivalent circuit with 6 elements including solution resistance $R_s$, capacitance $C_i$ and resistance $R_w$ of composite electrodes, adsorption capacitance $C_{ad}$, charge transfer resistance $R_{ct}$ and Warburg diffusion element $W$. It was found the lowest charge transfer resistance of 165.8Ω in the case of using 40 wt% TiO$_2$. The SEM images explained that the composite existed in uniform fiber with diameter size of nano range. It was found the presence of TiO$_2$ and PANi in material structure by X-ray diffraction and IR-spectra analysis, respectively.

Keywords. Ti/PANi-TiO$_2$ electrode, impedance spectroscopy, substrate electrolyte.

1. INTRODUCTION

Today, fossil fuels are becoming exhausted so the search for alternative energy sources is a matter of urgency. At the same time, environmental pollution problems are occurring with alarming levels. Microbial fuel cell (MFC) is device that generates electricity through the microbial biodegradation of organic compounds, as found in wastewater [1]. Therefore, microbial fuel cells are getting huge attention of researchers, in which the anode material is a major factor [2]. Polyaniline (PANi) is one of the famous conducting polymer because of its high electrochemical reversibility, high conductivity [3], easy preparation by both chemical way and electrochemical polymerization [4], good stability in air and environment. Titanium dioxide (TiO$_2$) is a special semiconductor with photocatalytic and hydrophilic properties which has shown to be a biocompatible stable material, however, with some modifications, its surface properties can be enhanced, varying from being a highly resistive to a lowly resistive material that composited with PANi as anode for MFC [5]. However, different methods resulting in obtaining that composite are opening for scientists.

In this work, PANi-TiO$_2$ composite was prepared by chemical method in paste form covered on titanium substrate using chitosan acetic acid solution as binder agent. The effects of TiO$_2$ content in composites on electrochemical behaviors were considered by cyclic voltammetry and electrochemical impedance measurement in brewery wastewater which is being a potential substrate electrolyte for MFC [6].

2. EXPERIMENTAL

2.1. Materials and preparation

Chemicals used in this study were provided by Merck (Germany) except aniline (from Kato Chemical, Japan) which was freshly distilled under vacuum before use. Titanium sheets as substrate electrodes were firstly polished by sandpaper grit of 180 and then pretreated for removing lubricant following procedure in [7]. The PANi-TiO$_2$ composites were prepared by chemical method using TiO$_2$ in sol gel form (from Institute of Applied Physics, VAST) which varied from 30 to 80 wt% to
aniline. Oxidative agent was ammoniumpersulfate (APS) in molar ratio to monomer of 1 to 1. The polymerization process was carried out under dropping APS solution and stirring at temperature of about 0-5 °C. The paste of those composites using 1% chitosan solution in acetic acid as binder agent was performed on pretreated titanium substrate and then tried at temperature of 120 °C for 2 h. Brewery wastewater (COD of 2100 mg/L) is used as electrolyte in this research for electrochemical measurements.

2.2. Detection method

The material structure analysis was carried out by infrared spectra on IMPACT 410-Nicolet unit. The morphology of material was examined by SEM on a equipment FE-SEM Hitachi S-4800 (Japan). The X-ray diffraction (XRD) of samples were obtained by X-ray diffractometer D8-Avance Bruker (Germany). The electrical conductivity measurement by I-E curve, cyclic voltammetry and electrochemical impedance spectroscopy (EIS) analysis were carried out on the electrochemical workstation unit IM6 (Zahner-Elektrik, Germany).

The conductivity $\delta$ (mS/cm) can be calculated through following equation [8]:

$$\delta = \frac{\Delta Ixd}{\Delta E}$$  \hspace{1cm} (1)

where $\Delta E$ is difference of potential (mV), $\Delta I$ is difference of responding current (mA) and $d$ is thickness of sample (cm).

3. RESULTS AND DISCUSSION

3.1. Material characterization

3.1.1. Electrical conductivity measurement

The data given in figure 1 and table 1 showed that a decrease of electrical conductivity obtained with increase of weight percent of TiO$_2$ to monomer during polymerization because of the low conductive TiO$_2$ intercalated into composite matrix. Among them the highest one for 40 wt% TiO$_2$ was found 13.37 mS/cm, however, this was only 40 $\mu$S/cm more than that for the case of 30 wt% TiO$_2$ indicating that no difference in electrical conductivity was found between composites using 30 or 40 wt% TiO$_2$. When TiO$_2$ over 40 wt% was used the conductivity decreased strongly and then slowly.

![Figure 1: I-E curves during electrical conductivity measurement of composites. Scan rate of 100 mV/s](image1)

**Table 1:** Effect of TiO$_2$ on electrical conductivity of composites

<table>
<thead>
<tr>
<th>Mass ratio of TiO$_2$ to aniline (%)</th>
<th>Conductivity $\delta$ (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>13.33</td>
</tr>
<tr>
<td>40</td>
<td>13.37</td>
</tr>
<tr>
<td>60</td>
<td>8.45</td>
</tr>
<tr>
<td>80</td>
<td>5.80</td>
</tr>
</tbody>
</table>

3.1.2. Morphology study

The SEM images on figure 2 indicated that the composite formed in big balls based on bundles of PANi fibers in the case of 30 wt% TiO$_2$ while it was observed in smaller ones if TiO$_2$ content of 40 wt% was used. This ball form was continuously modified by using TiO$_2$ of over 40 wt% indicating that it was a reason for decrease of electrical conductivity discussed above.

![Figure 2: SEM images of PANi-TiO$_2$ composite with different wt% TiO$_2$](image2)

The TEM images on figure 3 illustrated two different colors, among them the dark one belonging to anatase TiO$_2$ and the other bright one belonging to PANi fibers. SEM and TEM images explained that the PANi-TiO$_2$ existed in size of nanorange.
3.2. Electrochemical characterization

3.2.1. Potentiostatic polarization (PSP)

As we know brewery wastewater contains organic species and bacteria. When constant voltage is applied, it creates biological membrane on the surface of electrode. The higher response current density demonstrates the thicker biofilm is.

In this research, applied voltage was 450 mV in 60 minutes and the response current was measured with time. The figure 6 showed that the response current density on line 2 was the highest one with 40 wt% TiO$_2$ indicating the thickness biofilm was formed due to bacteria existed in electrolyte.

3.2.2. Electrochemical impedance study

The figure 7 illustrated Nyquist plots simulated following electrical equivalent circuits (EEC) on the figure 8 where solid lines are simulated ones which fitted well into symbol measured points. There are two different EEC, among them the first one with 7 elements (a) belongs to which measured before PSP and the other one with 6 elements belongs to which measured after PSP at 450 mV versus saturated calomel electrode (SCE).

The obtained data given on the table 2 and 3 demonstrated an important effect of TiO$_2$ not only on the both film capacitance ($C_f$) and resistance ($R_f$) of layer but also electrochemical process due to an appearance of adsorption resistance $R_{ad}$ and inductive element $L$ (figure 8a) as well as capacitance ($C_{ad}$) and Warburg diffusion element $W$ (figure 8b), respectively. There were found two electrochemical mechanisms occurred in the case without PSP stage, depending on TiO$_2$ content in composite. Among them the first one followed to EEC (b) with $W$ if TiO$_2$ content of 30-40 wt.% and...
the other one followed EEC (a) with an inductance element L that indicated probably a pseudo-inductive electro-chemical process assigning a relaxation effect which affects the conductivity [10] if TiO$_2$ content over 40 wt.%. However, after PSP stage it was found only one electrochemical mechanism occurred with EEC (b) for all TiO$_2$ content. It was found an increase of film capacitance

Figure 7: Effect of TiO$_2$ on Nyquist plots of composites measured in brewery wastewater (a) before and (b) after PSP at 450 mV. (Frequencie: 100 kHz÷10 mHz; Amplitude: 5 mV; COD = 2100 mg/L)

Figure 8: Electrical equivalent circuits of PANi-TiO$_2$ composite simulated from figure 7 before PSP stage (a,b) and after PSP stage (b)

(C$_0$), but, a decrease of film resistance (R$_f$) and Warburg diffusion coefficient (D) with raising of TiO$_2$ content in composites which affected on charge transfer resistance (R$_{ct}$). Among them the 40 wt% composite achieved the lowest R$_{ct}$. It means that the charge transfer process occurs most easily on the composite by using 40 wt% TiO$_2$. The diffusion element caused probably by bacteria and organic species from brewery wastewater using as substrate electrolyte which contributed to forming a biofilm on the electrode surface having the values in range of 10$^{-15}$ cm$^2$/s, however, they were slightly smaller than that in the case of 30-40 wt.% TiO$_2$ without PSP stage.

Table 2: Calculation of electrochemical parameters corresponding figure 7a simulated by schema on figure 8 before PSP stage

<table>
<thead>
<tr>
<th>Mass ratio of TiO$_2$/Ani</th>
<th>R$_s$ (Ω)</th>
<th>C$_f$ (nF)</th>
<th>R$_f$ (Ω)</th>
<th>CPE (nF)</th>
<th>C$_{ad}$ (µF)</th>
<th>R$_{ct}$ (kΩ)</th>
<th>R$_{ad}$ (Ω)</th>
<th>W</th>
<th>L (TH)</th>
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<tbody>
<tr>
<td>30</td>
<td>389.0</td>
<td>3.623</td>
<td>0.191</td>
<td>-</td>
<td>50.14</td>
<td>660.9</td>
<td>-</td>
<td>14.37</td>
<td>8.57</td>
</tr>
<tr>
<td>40</td>
<td>401.5</td>
<td>4.187</td>
<td>0.186</td>
<td>-</td>
<td>41.23</td>
<td>292.3</td>
<td>-</td>
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<tr>
<td>60</td>
<td>523.0</td>
<td>30650</td>
<td>1.179</td>
<td>3.116</td>
<td>-</td>
<td>495.3</td>
<td>1.132</td>
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<tr>
<td>80</td>
<td>354.7</td>
<td>50080</td>
<td>3.356</td>
<td>2.178</td>
<td>-</td>
<td>556.9</td>
<td>1.272</td>
<td>-</td>
<td>336.6</td>
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</table>

4. CONCLUSION

The PANi-TiO$_2$ composite was successfully synthesized by chemical method. The content of TiO$_2$ taken part in composites affected strongly on their electrochemical properties, among them the best one obtained by using 40 wt% TiO$_2$. The Warburg diffusion occurred after potentiostatic polarization stage due to a biofilm of bacteria existed in brewery wastewater.

Acknowledgements. This study was financially
Table 3: Calculation of electrochemical parameters corresponding figure 7b simulated by schema on figure 8b after PSP stage

<table>
<thead>
<tr>
<th>Mass ratio of TiO₂/Ani</th>
<th>$R_s$ (Ω)</th>
<th>$C_f$ (nF)</th>
<th>$R_f$ (Ω)</th>
<th>$C_{ad}$ (μF)</th>
<th>$R_{ct}$ (Ω)</th>
<th>W</th>
<th>$\sigma$ (Ωs$^{1/2}$)</th>
<th>D (10$^{-15}$ cm²/s)</th>
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<tr>
<td>30</td>
<td>423.8</td>
<td>4.333</td>
<td>200.2</td>
<td>38.19</td>
<td>298.6</td>
<td>24.57</td>
<td>2.93</td>
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<tr>
<td>40</td>
<td>397.3</td>
<td>3.750</td>
<td>171.9</td>
<td>33.49</td>
<td>165.8</td>
<td>23.20</td>
<td>3.29</td>
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<tr>
<td>60</td>
<td>391.5</td>
<td>4.590</td>
<td>191.6</td>
<td>23.98</td>
<td>585.4</td>
<td>39.73</td>
<td>1.12</td>
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</tr>
<tr>
<td>80</td>
<td>339.1</td>
<td>5.490</td>
<td>161.6</td>
<td>38.73</td>
<td>1510.0</td>
<td>127.00</td>
<td>0.11</td>
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REFERENCES


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