Vietnam Journal of Chemistry, International Edition, **55**(2): 158-162, 2017
DOI: 10.15625/2525-2321.2017-00436

Synthesis of PANi-TiO_2 composite and preparation of Ti/PANi-TiO_2 electrode for electrochemical study in brewery wastewater

Nguyen The Duyen[1,2,3], Mai Thi Xuan[1], Mai Thi Thanh Thuy[1], Nguyen Thi Van Anh[1], Phan Thi Binh[1,2*]

[1]*Institute of Chemistry, Vietnam Academy of Science and Technology*

[2]*Graduate University of Science and Technology, Vietnam Academy of Science and Technology*

[3]*Faculty of Chemistry, Hanoi Pedagogical University N[o]2*

Received 6 December 2016; Accepted for publication 11 April 2017

Abstract

PANi-TiO_2 composites are successfully by 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_f and resistance R_f 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 165.8 Ω 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 searchers, 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 electrochemistry 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 ^oC. 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 ^oC 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-Elecktrik, Germany).

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

$$\delta = \frac{\Delta I x d}{\Delta E} \quad (1)$$

where ΔE is difference of potential (mV), ΔI 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 μS/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.

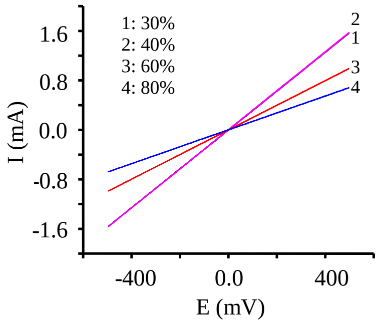


Figure 1: I-E curves during electrical conductivity measurement of composites. Scan rate of 100 mV/s

Table 1: Effect of TiO_2 on electrical conductivity of composites

Mass ratio of TiO_2 to aniline (%)	Conductivity δ (mS/cm)
30	13.33
40	13.37
60	8.45
80	5.80

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.

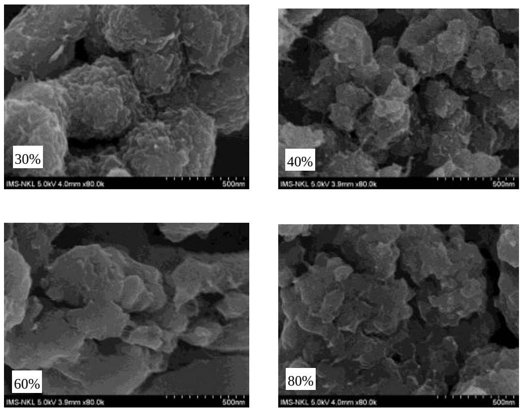


Figure 2: SEM images of PANi-TiO_2 composite with different wt% TiO_2

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.

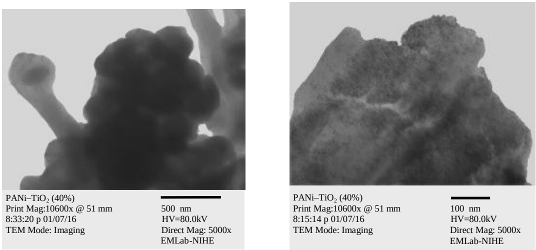


Figure 3: TEM images of PANi-TiO_2 composite with 40 wt% TiO_2

3.1.3. X-ray diffraction

The result from figure 4 showed that TiO_2 existed in anatase modification which posited in 2-Theta-Scale of 25.4, 37, 37.8, 48.1, 55 and 62.7 degree, while only one peak presented for PANi at about 26 ^{o}.

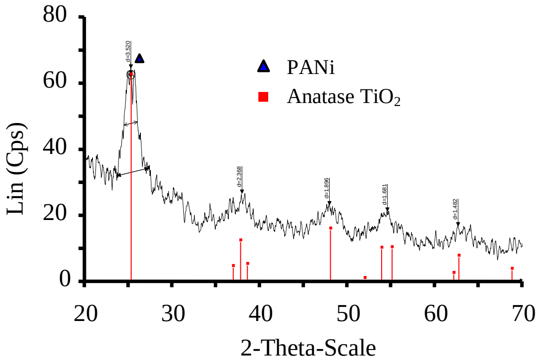


Figure 4: X-ray spectra of PANi-TiO_2 40 wt%

3.1.4. Infrared analysis

The results given in figure 5 explained that PANi existed in composite owing to vibration signals of benzoid and quinoid rings at 1571 and 1480 cm^{-1}, respectively [9]. Some other signals were found at 3490 cm^{-1} and 3383 cm^{-1} assigning N-H stretching mode, 2969 cm^{-1} and 2830 cm^{-1} (C-H), 1294 cm^{-1} (-N=quinoid=N-), 1104 cm^{-1} (C-N^+). It indicated that the obtained composite containing PANi in material matrix.

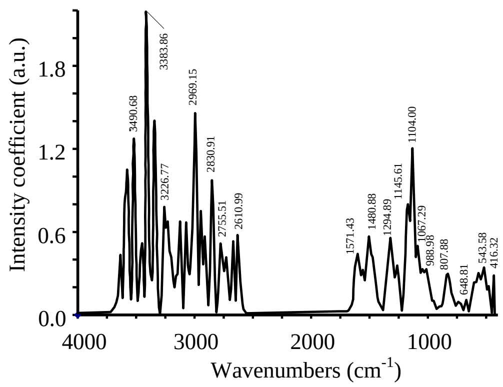


Figure 5: IR spectrum of PANi-TiO_2 composite

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.

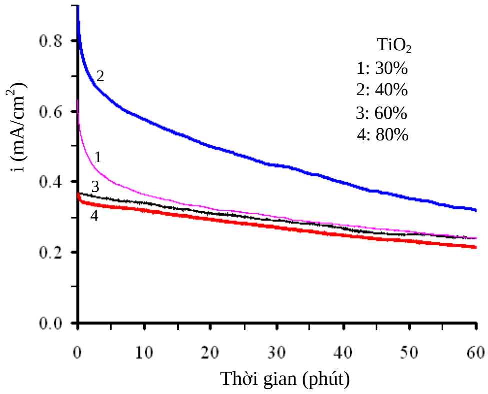


Figure 6: Effect of TiO_2 content on I-t curves at PSP (450 mV) in brewery wastewater (COD = 2100 mg/L)

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

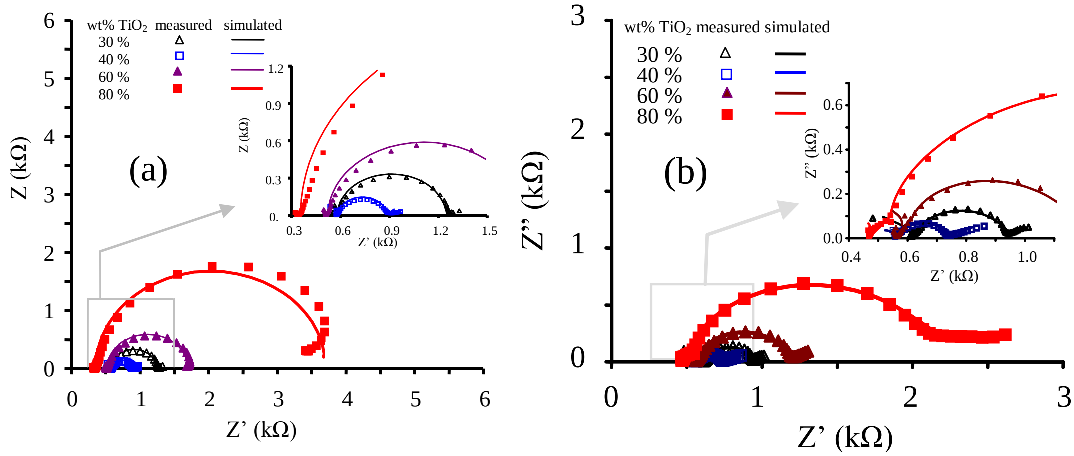
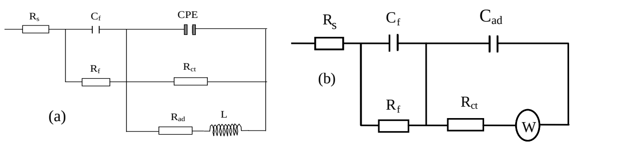


Figure 7: Effect of TiO_2 on Nyquist plots of composites measured in brewery wastewater (a) before and (b) after PSP at 450 mV.
(Frequence: 100 kHz÷10 mHz; Amplitude: 5 mV; COD = 2100 mg/L)



R_{ct}: Charge transfer resistance
C_{ad}: Adsorption capacitance
W: Warburg diffusion element
R_s: Solution resistance
C_f: Capacitance of composite layer
R_{ad}: Adsorption resistance
CPE: constant phase element
L: Inductive element
R_f: Resistance of composite layer

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_f), 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

Mass ratio of TiO_2/Ani	R_s (Ω)	C_f (nF)	R_f (Ω)	CPE (nF)	C_{ad} (µF)	R_{ct} (kΩ)	R_{ad} (Ω)	W		L (TH)
								σ ($Ω.s^{-1/2}$)	D (10^{-15} cm^2/s)	
30	389.0	3.623	0.191	-	50.14	660.9	-	14.37	8.57	-
40	401.5	4.187	0.186	-	41.23	292.3	-	17.32	5.89	-
60	523.0	30650	1.179	3.116	-	495.3	1.132	-	-	267.3
80	354.7	50080	3.356	2.178	-	556.9	1.272	-	-	336.6

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* *supported by the NAFOSTED of Vietnam under code number 104.99-2013.44.*

Table 3: Calculation of electrochemical parameters corresponding figure 7b simulated by schema on figure 8b after PSP stage

Mass ratio of TiO_2/Ani	R_s (Ω)	C_f (nF)	R_f (Ω)	C_{ad} (μF)	R_{ct} (Ω)	W	
						σ ($\Omega.s^{-1/2}$)	D (10^{-15} cm^2/s)
30	423.8	4.333	200.2	38.19	298.6	24.57	2.93
40	397.3	3.750	171.9	33.49	165.8	23.20	3.29
60	391.5	4.590	191.6	23.98	585.4	39.73	1.12
80	339.1	5.490	161.6	38.73	1510.0	127.00	0.11

REFERENCES

1. B. E. Logan, J. M. Regan. *Microbial fuel cells-challenges and applications*, Environ. Sci. Tech., **40**, 5172-5180 (2006).
2. K. Scott, G. A. Rimbu, K. P. Katuri, K. K. Prasad, I. M. Head. *Application of modified carbon anodes in Microbial fuel cells*, Process Safety and Environmental Protection, **85(B5)**, 481-488 (2007).
3. Y. Qiao, B. Shu-Juan, C. Ming Li, C. Xiao-Qiang, L. Zhi-Song, G. Jun. *Nanostructured Polyaniline Titanium Dioxide Composite Anode for Microbial Fuel Cells.* ACS NANO, **2**, 113-119 (2008).
4. D. D. Bore, U. R. Kapadi, P. P. Kumbhar, D. G. Hundiwale. *Influence of inorganic and organic supporting electrolytes on the electrochemical synthesis of polyaniline, poly (o-toluidine) and their copolymer thin films,* Materials Letter, **56**, 685-691 (2002).
5. V. E. Henrich. *The Surface Science of Metal Oxides*. Cambridge University Press (1996).
6. Y. Feng, X. Wang, B. E. Logan, H. Lee. *Brewery wastewater treatment using air-cathode microbial fuel cells,* Appl. Microbiol. Biotechnol., **78**, 873-880 (2008).
7. Thi Tot Pham, The Duyen Nguyen, Thi Xuan Mai, Thi Thanh Thuy Mai, Hai Yen Tran and Thi Binh Phan. *Influence of polyaniline on photoelectrochemical characterization of TiO2-PANI layers.* Adv. Nat. Sci.: Nanosci. Nanotechnol. 6 (2015) 025008 (5pp). DOI: 10.1088/2043-6262/6/2/025008.
8. Phan Thi Binh. *Electrochemical polymerization of aniline by current pulse method in the presence of m-aminobenzoic acid in chlorhydric acid solution.* Macromol. Symp., **249-250**, 228-233 (2007) DOI: 228 10.1002/masy.200750337.
9. I. A Abd.Razak, A. L. Ahmad and S. H. Sharif. Zein. *Polymerisation of protonic polyaniline/multi-walled carbon nanotubes-manganese dioxide nanocomposites* J. Phys. Sci., **20**, 27-34 (2009).
10. Phan Thi Binh, Mai Thi Xuan, Nguyen The Duyen, Pham Thi Tot, Mai Thi Thanh Thuy, Nguyen Thi Van Anh, Tran Dai Lam. *Improving electrochemical behavior of sustainable polyaniline titanium dioxide composite by intercalation of carbon nanotubes.* Green Processing and Synthesis, **5(6)**, 549-556 (2016). DOI: 10.1515/gps-2016-0109.

Corresponding author: **Phan Thi Binh**
Institute of Chemistry
Vietnam Academy of Science and Technology
No 18, Hoang Quoc Viet, Cau Giay District, Hanoi
E-mail: phanthibinh@ich.vast.vn.