VIETNAM JOURNAL OF CHEMISTRY VOL. 53(2) 170-173 APRIL 2015
DOI: 10.15625/0866-7144.2015-00109

ELECTROCHEMICAL IMPEDANCE STUDY ON NANOSTRUCTURED TITANIUM DIOXIDE POLYANILINE COMPOSITE PREPARED BY CYCLIC VOLTAMMETRY

Nguyen The Duyen[1], Phan Thi Binh[2*]

[1]*Faculty of Chemistry, Hanoi Pedagogical University N°2*

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

Received 25 December 2015; Accepted for Publication 20 April 2015

Abstract

In this study, electrochemical impedance of nanostructured titanium dioxide polyaniline composite prepared by cyclic voltammetry was investigated and suggested an equivalent circuit in which 5 elements taken part, such as R_s represents the electrolyte resistance, C_{CPE} represents the constant phase element, C_Y represents the young's surface layer impedance, R_f and C_f represent the resistance and capacitance of material film, respectively. The results showed that the more TiO_2 takes part in synthesis solution the bigger electrochemical impedance receives the composite, the more cyclic number carried out during synthesis of material the larger Nyquist cirle from which becomes.

Keywords. Nanostructured TiO_2-PANi composite, electrochemical impedance, impedance simulation.

1. INTRODUCTION

Titanium oxide polyaniline (TiO_2-PANi) is a potential composite for electrochemical application in the praxis. It can be hybrided by many ways, such as chemical, electrochemical or enzymatic synthesis [1-4]. A large number of studies on those composite materials have been reported, most of their researches are still focusing on the preparation of materials and characterization [5,6], such as morphology and chemical structures as well as electrochemical properties [3,7], such as electrochemical impedance and cyclic polarization. But a few reports evaluated their electrochemical impedance, when thickness of the composite film varied by cyclic number during synthesis.

In this paper, the Ti/TiO_2-PANi electrodes were prepared by cyclic voltammetry under variation of cyclic number from 50 to 150 during synthesis and mass ratio of TiO_2 to aniline from 1/6 to 1/12. Their electrochemical impedance was analysed and evaluated in comparison with polyaniline (PANi) film.

2. EXPERIMENTAL

2.1. Material preparation

All chemicals used in this study were provided by Merck (Germany). Aniline was freshly distilled under *vacuum* before use. The titanium electrodes were polished by sandpaper with 2000 grit and then removed lubricant from their surface by distilled water and then cleaned by cyclic voltammetry under scan rate of 100 mV/s in 0.5 M H_2SO_4 solution. The TiO_2-PANi composites were synthesized from mixed solution of 0.1 M H_2SO_4 + 0.1 M Aniline + TiO_2 sol by cyclic voltammetry under variation of cycle number from 50 to 150 and mass ratio of TiO_2 to aniline from 1/6 to 1/12 at scan rate of 20 mV/s in the potential area of 0.4÷1.1V on the electrochemical workstation unit IM6 (Zahner-Elecktrik, Germany).

2.2. Detection method

The morphological structure of materials was carried out by TEM on a Jeol 200CX (Japan). The impedance measurement of materials was carried out in 0.5 M H_2SO_4 at amplitude of 5 mV in the frequency area of 10 mHz÷100 kHz. The impedance simulation was done for evaluation of influence of film thickness on impedance parameter of materials.

Diffusion coefficient D was calculated by the following formulation [8,9]:

$$D = \frac{2R^2T^2}{n^4F^4A^2C^2\sigma^2} \tag{1}$$

where σ –Warburg constant ($\Omega s^{-1/2}$); A- electrode surface area (cm^2); n – exchange electron number in the charge transfer process; T–absolute temperature (K), R–Boltzman gas constant (8.314 J/mol.K; F - Faraday constant (96.500 As); C- oxidant/reductant concentration of titanium in the electrode material (=1 mol/cm^3).

3. RESULTS AND DISCUSSION

3.1. Morphological study

There was found on TEM images (Fig. 1) two different colours among them the light one belonging to PANi enclosing the dark one belonging to TiO_2 which forming together in nanostructured composite. The obtained result explained that nanostructured composites based on TiO_2 and PANi were successfully prepared by cyclic voltammetry method.

3.2. Study on electrochemical impedance spectroscopy (EIS)

The data given on figure 2 showed that the measurement data (symbols) fitted good into simulation data (solid lines) following equivalent circuit (d) which was found with 5 elements, where R_s represents the electrolyte resistance, C_{CPE} represents constant phase element, W represents a Warburg diffusion as a part of a charge transfer reaction, R_f represents the resistance of material film and C_Y represents the young's surface layer impedance. The results expressed that the more cyclic number used for synthesis of material the bigger electrochemical impedance had the material because of thicker film formed, the smaller mass ratio between TiO_2 and aniline used the smaller electrochemical impedance had the material also (figure 2 and tables 1 to 3). Conversely, capacitance of PANi and composite film increased with raising of cyclic number during synthesis, however, compared with PANi film, the capacitance of composite was smaller, except the case of composite B (1/12) prepared under 50 cycle. It was found nearly no big different value of the constant phase element C_{CPE} (table 3) in the case of applying 150 cycles.

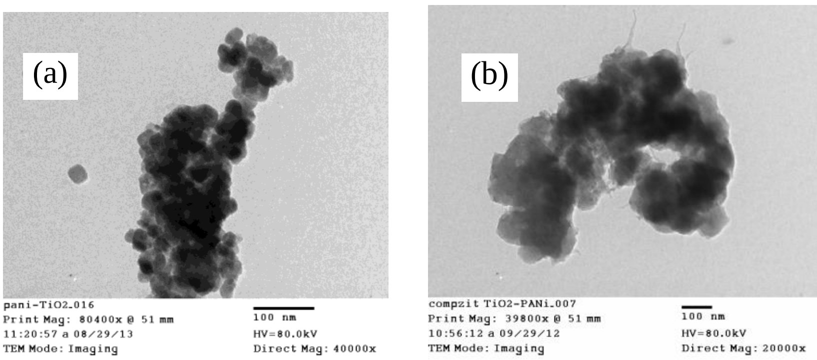

Fig. 1: TEM image of TiO_2-PANi composite (a) (A: ratio 1/6) and (b) (B: ratio 1/12)

Table 1: Electrochemical parameters corresponding figure 2 estimated from fitting of experimental data to schema shown in figure 2a (50 cycles)

Materials	R_s (Ω)	C_{CPE}		C_Y			R_f (kΩ)	W	
		(μF)	(m)	(mF)	p	τ (Gs)		σ ($\Omega/s^{1/2}$)	D (cm^2/s)
Composite A (1/6)	3.314	2.413	0.938	0.670	0.146	269.1	1.010	159.7	0.56×10^{-18}
Composite B (1/12)	2.523	2.330	0.917	4.292	0.142	419.3	1.221	131.4	0.83×10^{-18}
PANi	3.274	2.467	0.935	1.890	0.146	269.1	0.716	156.6	0.59×10^{-18}

Table 2: Electrochemical parameters corresponding figure 2 estimated from fitting of experimental data to schema shown in figure 2b (100 cycles)

Materials	R_s (Ω)	C_{CPE}		C_Y			R_f (kΩ)	W	
		(μF)	(m)	(mF)	p	τ (Gs)		σ ($\Omega/s^{1/2}$)	D (cm^2/s)
Composite A (1/6)	2.552	2.327	0.930	2.811	0.146	269.1	2.532	169.6	$0.50x10^{-19}$
Composite B (1/12)	2.705	2.229	0.922	5.885	0.146	269.1	2.302	241.1	$0.25x10^{-19}$
PANi	3.233	1.661	0.918	5.693	0.146	269.1	1.741	117.5	$1.04x10^{-19}$

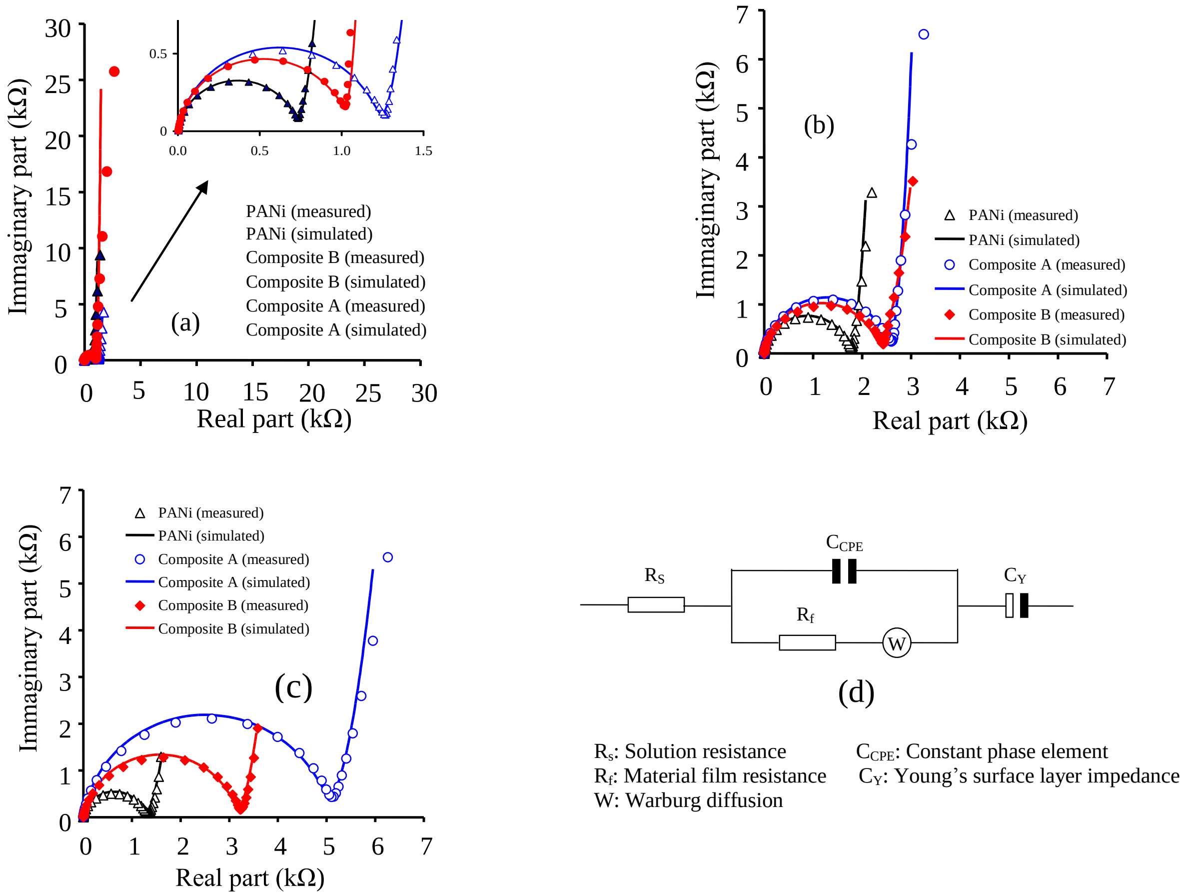

Figure 2: Nyquist diagrams of TiO_2-PANi composites prepared under different conditions (mass ratio of TiO_2 to aniline: 1/6 (composite A) and 1/12 (composite B)) compared with PANi film. Cyclic number during synthesis of materials: a): 50, b) 100 and c) 150; equivalent circuit (d)

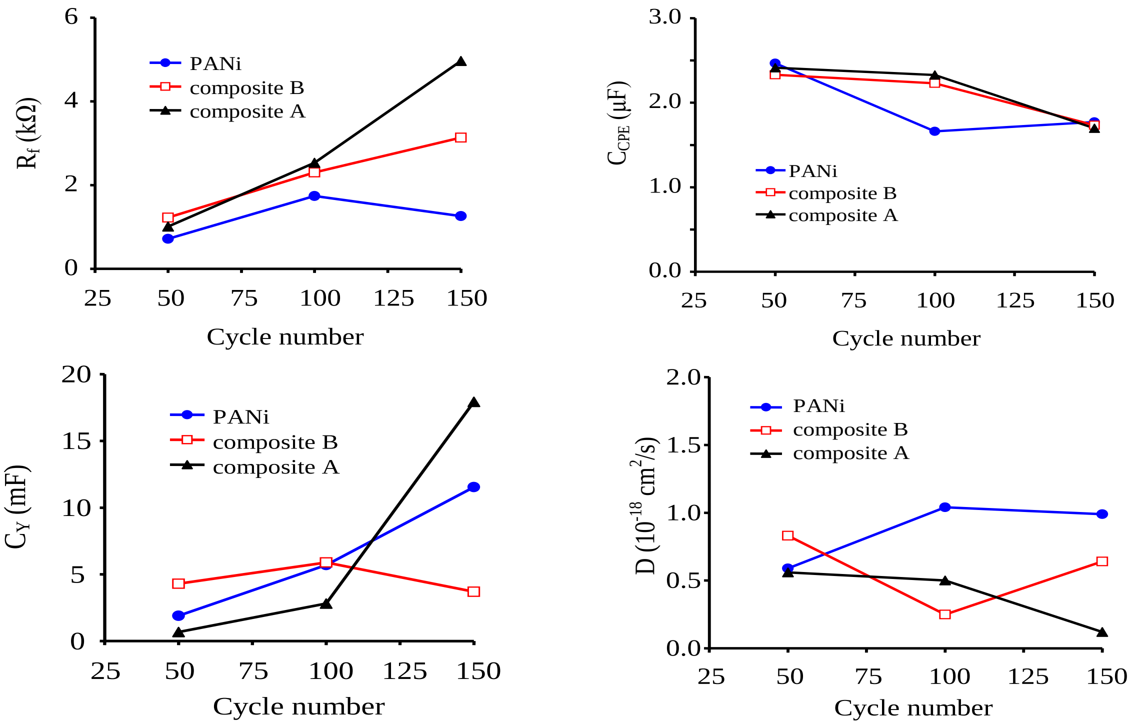

Figure 3: The dependence of some fitting electrochemical parameters on cyclic number applying in synthesis process of materials. The mass ratio of TiO_2 to aniline: 1/6 (composite A) and 1/12 (composite B)

Table 3: Electrochemical parameters corresponding figure 2 estimated from fitting of experimental data to schema shown in figure 2c (150 cycles)

Materials	R_s (Ω)	C_{CPE}		C_Y			R_f (kΩ)	W	
		(μF)	(m)	(mF)	p	τ (Gs)		σ ($\Omega/s^{1/2}$)	D (cm^2/s)
Composite A (1/6)	3.112	1.698	0.916	3.693	0.146	269.1	4.964	351.0	$0.12x10^{-19}$
Composite B (1/12)	3.953	1.733	0.898	11.540	0.146	269.1	3.133	149.8	$0.64x10^{-19}$
PANi	3.584	1.771	0.909	17.920	0.146	269.1	1.258	120.4	$0.99x10^{-19}$

Young's surface layer impedance is element describing a passive layer with conductivity penetrating from one side and decaying exponentially [10] for which the three parameters can be shown such as dimensionless p (relative penetration depth of the conductivity within the dielectric), time constant τ (built from a slice of the dielectric with its capacity and resistance at the site of the highest conductivity) and total capacity C_Y (of the layer neglecting the conductivity).

It was found that all materials had the same value of p (0.146) and τ (269.1 Gs) except composite B (1/12) prepared by 50 cycles. The reason for it may be explained that the TiO_2 makes influence on which only when the material film is still thin. Compared with PANi, the composite prepared under the same condition of 150 cycles had very lightly difference in C_{CPE}, but larger difference in R_f, C_Y and D caused not only by the thickness of material film but also the mass ratio between TiO_2 and aniline of synthesis solution following which R_f increased, C_Y and D decreased (figure 3).

4. CONCLUSIONS

From above results we conclude that nanostructured TiO_2-PANi composite was prepared successfully by cyclic voltammetric method. The more cyclic number applied for synthesis of material the bigger electrochemical impedance received material, the smaller mass ratio between TiO_2 and aniline used the smaller impedance value received material. Nearly no big different value of the constant phase element (C_{CPE}) was found, but there was found big difference for material film resistance (R_f), young's surface layer impedance (C_Y) and Warburg diffusion coefficient (D) in the case of applying 150 cycles during synthesis of materials.

Acknowledgements. *This study was financially supported by the NAFOSTED of Vietnam under code number 104.99-2013.44. The authors would like to thank the Humboldt-Fellowship for the support of the IM6 equipment.*

REFERENCES

1. Akash Katoch, Markus Burkhart, Taejin Hwang, Sang Sub Kim. *Synthesis of polyaniline/TiO$_2$ hybrid nanoplates via sol-gel chemical method.* Chemical Engineering Journal, 192, 262-268, 2012
2. Duong Ngoc Huyen, Nguyen Trong Tung, Nguyen Duc Thien and Le Hai Thanh. *Effect of TiO$_2$ on the Gas Sensing Features of TiO$_2$/PANi Nanocomposites,* Sensors, **11(2)**, 1924-1931 2011. doi: 10.3390/s110201924.
3. C Cristescu, A. Andronie, S. Iodrache, S.N. Stamatin, L. M. Constantinescu, G. A. Rimbu , M. Iodroc, R. Vasilescu-Mirea, I. Iodrche, I. Stamatin. *PANi - TiO$_2$ nanostructures for fuel cell and sensor applications.* J.Optoelectronics and Advanced Materials, **10(11)**, 2985-2987 2008.
4. Mohammad Reza Nabid, Maryam Golbabaee, Abdolmajid Bayandori Moghaddam, Rassoul Dinarvand, Roya Sedghi. *Polyaniline/TiO$_2$ nanocomposite,* Int. J. Electrochem. Sci., **3**, 1117-1126 (2008).
5. V. E. Henrich. *The Surface Science of Metal Oxides. Cambridge University Press,* 1996. ISBN-10: 0521566878.
6. S. G. Pawar, S. L. Patil, M. A. Chougule, B. T. Raut, D. M. Jundale and V. B. Patil. *Polyaniline:TiO$_2$ composites: Synthesis and characterization.* Archives of Applied Science Research, 2 (2) 194-201 (2010).
7. Al-Nakib Chowdhury and Mosharrefa Akter. *Electrochemical preparation, redox behaviour and stability of some electroactive films having organic/ organic and organic/inorganic hybrid structures.* Asian Journal of Chemistry, **19(2)**, 843-854 (2007).
8. F. Richter. Basic and application. IM6/6ex Manual, Zahner Rlektrik, Germany.
9. N. Wagner. *Application of electrochemical impedance spectroscopy for fuel cell characterization: polymer electrolyte fuel cell (pefc) and oxygen reduction reaction in alkaline solution.* Bulgarian Chemical Communications, **44(4)**, 371-382 (2012).
10. H. Göhr, C. A. Schiller. *Faraday-Impedanz als Verknüpfung von Impedanzelementen.* Z. Phys. Chem. Neue Folge, **148**, 105-124 (1986).

Corresponding author: **Phan Thi Binh**
Institute of Chemistry, Vietnam Academy of Science and Technology
18 Hoang Quoc Viet, Cau Giay, Hanoi. E-mail: phanthibinh@ich.vast.vn.