The preparation of composites between polyaniline-silver (PANI-Ag) via interfacial polymerization

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Abstract. In this study, polyaniline-silver (PANI-Ag) composites between aniline monomer and Ag particles in silver nitrate were prepared via interfacial polymerization method at room temperature. The objective was to study the effects of mass ratios of aniline monomer to Ag particles in silver nitrate (1:0.5, 1:1, 1:1.5, 1:2 and 1:2.5) on the electrochemical properties. The characterization techniques included FTIR, XRD, SEM and EDAX. FTIR and XRD results presented the success of the synthesis of the composites and crystallization of the PANI-Ag composites due to the presence of silver. SEM and EDAX techniques indicated that polyaniline nanofibers were successfully covered on the Ag particles. The CV results showed the higher specific capacitance with increasing amounts of Ag particles.

1. Introduction

Nowadays, devices for storing electrical energy which are batteries and capacitors are widely used in electrical industries. However, the process of charge-discharge electricity in batteries take quit a long time and limiting the usage in many applications. Therefore, the researchers are currently interested in studying and developing the capacitors to be more capacitance and electrical energy storage. Capacitors can charge-discharge electricity very quickly than batteries. Generally, the electrodes are produced from carbon materials (carbon nanotubes (CNTs)), transition metal oxide (NiO, Co3O4, MnO2, TiO2, SnO2 and CuO) [1-7] and conducting polymers are simple chemical and electrochemical synthesis, economical price and high environmental stability.

Among conductive polymer, polyaniline (PANI) has gained more attention to produce electrode due to there are 4 oxidation states (leucoemeraldine, emeraldine base, emeraldine salt and pernigraniline). It has high specific capacitance pseudocapacitor. Although conductive state of PANI is only green protonated emeraldine. On the other hand, PANI has lower conductivity than metal. Thus, the researchers try to improve electrical properties of PANI via metal doping method. Silver particle (Ag) is transition metal, there are high electrical properties and high surface area. After electrode synthesis, Ag particle can reduce electrical resistivity or charge transfer resistance. [8]

Therefore, different methods have been used to improve capacitors properties. In the Interfacial polymerization technique, the polymerization is occurred in immiscible organic/aqueous biphasic system. This technique no add surfactant, simply synthesize and variety of organic solvent. Recently, Mahesh D. Bedre et al. prepared PANI-Ag nanocomposites via employing interfacial polymerization using ammonium persulphate as an oxidizing agent. Resulting in the reduction of Ag⁺ to Ag⁰ and to
conducting emeraldine salt.[9] Ahmad Abdolahi et al. synthesized PANI-Ag composites with core-shell structure by interfacial polymerization method.[10] Kuk Ro Yoon et al. synthesized polypyrrole-silver (PPy-Ag) nanocomposites by aqueous polymerization (PPy-Ag-Aq) and interfacial polymerization (PPy-Ag-IF). The silver particles were dispersed in PPy-Ag-IF better than in PPy-Ag-Aq.[11]

In this research, the PANI-Ag composites use addition of Ag in PANI to reduce electrical resistance and to enhance the electrochemical properties. The transition metal particles are widely used due to the presence of unique magnetic, optical and catalytic properties. The electrodes was based on the current composite materials were prepared via interfacial polymerization by dispersing silver particles and aniline monomer in the water phase and inorganic phase, respectively. The objectives of this work is to study morphology and electrochemical properties of PANI-Ag composites.[10]

2. Experimental

2.1. Materials
Aniline monomer (LOBA CHEMI PVT.LTD) purchased from India, silver nitrate (POCH) purchased from Poland, ammonium persulphate (Ajax Finechem Pty.Ltd) purchased from Poland Ausrtalia, chloroform (ACl Lacscan) purchased from Thailand and sulfuric acid (EMSURE GO made in Germany).

2.2. Synthesis of polyaniline-silver composites
The synthesis of composite materials between polyaniline and Ag particles from interfacial polymerization by preparing solutions with 2 systems. The first system is organic phase by put 0.36 ml of aniline monomer in 20 ml of chloroform and the second system is silver nitrate in distilled water by mixed 0.23 g of ammonium persulfate with 0.2 g of silver nitrate in10 ml of sulphuric acid (1 M) after that mixed and stirred solution each system for 30 minutes. The mixing 2 systems, pour the second system into the first system and leave for interfacial polymerization for 24 hours then filtered and washed with acetone and distilled water. It will turn into a precipitate and colorless solution. Finally dried for 48 hours. PANI-Ag composites with different mass ratio of Ag particles in silver nitrate (1:0.5, 1:1, 1:1.5, 1:2 and 1:2.5).

2.3. Characterizations
PANI-Ag composites were characterized by fourier transform infrared spectroscopy (FTIR) (NICOLET, Impact, United States), x-ray diffraction (XRD) (SHIMADZU, Lab X, XRD 6100, Japan), scanning electron microscopy (SEM) (MIRA3 TESCAN, Australia) of composites sputtered coated with Pd/Au.

2.4. Preparation and characterization of the electrode
The electrochemical analysis of PANI-Ag composites was carried out through the standard three-electrode cell configuration. The counter electrode was platinum wire, the reference electrode was Ag/AgCl and the working electrode was prepared by mixing 80 %w/w of the PANI-Ag composites, 10 %w/w of carbon black (Vulcan XC 72R) and 10 %w/w of polyvinylidene fluoride. The mixture was dissolved in 1-methyl-2-pyrrolidinone (NMP) solvent, then drop coated onto the glassy carbon electrode (GCE). The prepared GCE working electrode was dried at 80 °C for 24 hours to eliminate the solvent.[11] The CV test using DY2311 Potential (Digi-Ivy, Inc, United States) and the electrolyte was 1M H₂SO₄ solution and all the electrochemical analyses were tested at room temperature.
3. Results and discussion

3.1. Fourier transform infrared spectroscopy

The FTIR spectra of pure PANI and PANI-Ag composites were recorded and shown in Figure 1. Pure PANI and PANI-Ag composites has the main peaks at 1108.98 cm\(^{-1}\), 1478.74 cm\(^{-1}\) and 1559.57 cm\(^{-1}\) associated with C=N and C=C stretching of quinoid and benzenoid rings in the polyaniline structure. The peak at about 3228.53 cm\(^{-1}\) is O-H stretching from HNO\(_3\) and not presented in pure PANI. Based on FTIR results, it could be confirmed that polyaniline was successfully synthesized due to the characteristic peaks corresponding to emeraldine salt (ES) is 3138.82 cm\(^{-1}\), 1559.57 cm\(^{-1}\), 1478.74 cm\(^{-1}\), 1294.30 cm\(^{-1}\) and 1238.45 cm\(^{-1}\).[9,10]

3.2. X-ray diffraction

The XRD patterns of PANI-Ag composites are presented in Figure 2. The Figure 2a showed only broad peak at about 20 value of 10-35°. This is the characteristic peak of PANI corresponded to amorphous nature of PANI. The results. In the PANI-Ag composites indicated the appearance of the FCC structure of...
Ag particles, as indicated by the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) diffraction peaks ($2\theta$) at 38.1°, 44.2°, 64.3° and 77.5°, respectively. As a result, All peak of PANI-Ag composite match with the JCPDS file 04-0783 of Ag. [9]

3.3. Scanning electron microscopy

![Figure 3. SEM images of the PANI-Ag composites](a) Pure PANI, (b) PANI-Ag0.5, (c) PANI-Ag1.0, (d) PANI-Ag1.5, (e) PANI-Ag2.0 and (f) PANI-Ag2.5.]

The morphology of PANI-Ag composites is shown in Figure 3. Normally, three stages are proposed in PANI synthesis: 1) nucleation, 2) initial growth, 3) secondary growth. Figure 3a, in interfacial polymerization form only PANI nanofiber in initial growth stage. It is proposed the secondary growth stage is suppressed due to the secondary growth stage leads to PANI in micro-size scale. [8] From Figure 3b-f shown the formation of polyaniline nanofibers with surface roughness. However, increasing Ag contents found more gap between polyaniline nanofibers. From Figure 3e, PANI-Ag2.0 exhibited the formation of polyaniline nanofibers and sheets. From Figure 3f, PANI-Ag2.5 found the smallest polyaniline nanofibers compared to other Ag contents. Thus, SEM images indicated the interfacial polymerization caused the formation of aniline monomer on Ag particles that act as the growth centers and Ag particles are covered with a layer of polyaniline nanofibers.[9,10]
Figure 4. EDAX images of the PANI-Ag composites (a) PANI-Ag0.5, (b) PANI-Ag1.0, (c) PANI-Ag1.5, (d) PANI-Ag2.0 and (e) PANI-Ag2.5 and (f) EDAX mapping.

The study of elemental compositions using the EDAX technique are shown in Figure 4. From Figure 4a-e, presented the dispersion of Ag particles in PANI as a matrix. Figure 4d, PANI-Ag2.0 is the most dispersion and distribution and Figure 4e, PANI-Ag2.5 exhibited agglomeration of Ag particles in the PANI matrix because of Ag particles content increasing. The EDAX mapping, Figure 4f, presented %elements of carbon, nitrogen, oxygen and silver.[12]

3.4. Cyclic voltammetry

Figure 5. Cyclic voltammograms of the PANI-Ag composites (a) Pure PANI, (b) PANI-Ag0.5, (c) PANI-Ag1.0, (d) PANI-Ag1.5, (e) PANI-Ag2.0 and (f) PANI-Ag2.5 in 1M H$_2$SO$_4$

The results of the study of electrical properties of pure PANI and PANI-Ag composites using the CV technique are shown in Figure 5, at potential range of -1 to +1 V and using 1M H$_2$SO$_4$ as the electrolyte at scan rate is 50 mV/s. Figure 5a, pure PANI didn’t presented redox reaction and low specific capacitance. Figure 5b-c, PANI-Ag0.5 and PANI-Ag1.0 presented only reduction reaction peak and no
oxidation reaction peak. In PANI-Ag composites synthesis when Ag particles content increasing, will show oxidation and reduction reaction peak that indicated transition metal (silver) can occur redox reaction which is pseudocapacitors characteristics. The composite materials in different Ag particles content, Ag particles content increasing found the area under the CV curves increasing and specific capacitance also increasing. The specific capacitances of PANI-Ag composites were calculated from equation 1[12], and the results were shown in Table 1:

\[ C_{sp} = \frac{\int_{V_i}^{V_f} I|dV}{2 \times \Delta V \times m \times SR} \]  

(1)

Where the integral part in the numerator gives the area under the CV curve, \( \Delta V \) is the potential range, \( I \) is the applied current, \( m \) is the weight of the deposited PANI-Ag composites on GCE and SR is scan rate.[12]

| Composites   | Specific capacitance (F/g) |
|--------------|----------------------------|
| Pure PANI    | 18.84                      |
| PANI-Ag0.5   | 58.84                      |
| PANI-Ag1.0   | 61.34                      |
| PANI-Ag1.5   | 185.17                     |
| PANI-Ag2.0   | 385.67                     |
| PANI-Ag2.5   | 276.94                     |

4. Conclusion

The preparation of PANI-Ag composites with various silver contents was successful through the interfacial polymerization method. This could be confirmed by the FTIR results, which showed peaks attributed to the functional groups in the polyaniline structure and XRD analysis indicated the crystalline formation of Ag particles, which was confirmed by the presence of sharp peaks. The XRD board peak suggested the amorphous nature polyaniline. In accordance with SEM micrographs, observed PANI formation in Ag particles which act as the growth centers. From studying the dispersion of Ag particles in PANI and compositions of elements with EDAX technique, it was found that PANI-Ag2.0 had the most dispersion and distribution. The results of EDAX were in consistent corresponding with CV technique. The specific capacitance of PANI-Ag2.0 was optimal with the value of 385.67 F/g.

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