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Research article

Multiwalled Carbon Nanotube/PEDOT: PSS Coated on Pineapple Fiber Paper Based Flexible Electrode for Electrochemical Application

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Abstract

Keywords

green electrode;

pineapple fiber paper;

flexible electrode

In this study, a green electrode made from natural fiber paper was investigated. A pineapple fiber paper was used as electrode support material. A mixture of multiwalled carbon nanotubes and PEDOT: PSS (MWCNTs/ PEDOT: PSS) was used as active electrode material. PEDOT: PSS, a conducting polymer, was applied as binder to connect between MWCNTs and the surface of pineapple fiber paper, and this setup showed decrease in electrode resistivity. Varying the MWCNT concentration mixed with PEDOT: PSS on pineapple fiber paper was explored. The 3 wt.% MWCNT device gave the maximum conductivity value of 10.87 S cm^{-1}. Cyclic voltammetry and impedance analysis indicated that 3 wt.% MWCNT device showed considerable promise as a flexible electrode for electrochemical devices for energy storage applications.

1. Introduction

Flexible electrodes have attracted much attention in the energy storage field such as lithium-ion batteries [1] and electrochemical capacitors [2, 3]. This is due to their promising properties, i.e. being flexible, portable, lightweight, and bendable. Some natural fibers are good candidates for flexible electrode substrate materials because they can be formed into carbon structures with hollow pores and good electrical conductivity [3]. Pineapple is one of the largest agricultural products in Thailand. From 2008 to 2018, Thailand produced an average of 2,096.44 thousand tonnes/year of pineapples [4]. This production created a large volume of plant-based wastes. A large amount of

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that came from the pineapple leaves, which contain a high content of natural fiber. The use of pineapple leaves as a promising source of fiber has an advantage of being inexpensive, abundant, and biodegradable, and having high tensile strange and high young modulus value [5, 6].

Typically, electrodes for energy storage applications consist of carbon-based anodes and transition metal oxide cathodes. Metal foil is usually used as a conductive substrate and structural supporter because of its electrical properties and flat surface. However, metal foil has low resistance to corrosion in some electrode systems leading to an increase of internal impedance [7]. Compared with metal-based electrodes, paper electrodes have an advantage in terms of chemical stability and offer other benefits such as low cost, light weight, environmental friendliness, recyclability, and bendability. However, paper has poor electrochemical performance. To improve it, chemical treatment [8] or additives have been applied to raw carbon fiber paper. With chemical treatment, the areal capacitance of carbon fiber paper can be improved up to 1275 mF cm^{-2} [8]. For additive addition, carbon nanotube (CNT), graphene, and carbon fiber have been applied to enhance the electrical conductivity of the paper. Among these, paper with added CNT showed promising electrochemical performance for use as electrode materials due to its mechanical strength, high conductivity, chemical stability, and because of the large surface area of CNTs [9, 10]. CNTs have generally been applied to the anode electrodes for lithium-ion batteries [11]. Various methods to fabricate paper electrodes are printing or drawing, soaking and polymerization, vaporization and vacuum filtration [11]. However, the printing method shows a low cost and is simple.

Poly (3, 4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT: PSS) is a conducting polymer widely used as a binder in electrochemical electrodes [12]. This is because PEDOT: PSS has the properties of flexibility, high electrical conductivity, electrochemical stability and hydrophobicity [13]. Furthermore, PEDOT: PSS has a conjugated backbone along with delocalized electrons that can easily migrate, which is an important property for a charge storage material [13]. The conducting polymer has frequently been employed coupled with CNTs in electrodes in energy storage systems. For example, single-wall carbon nanotubes (SWCNTs) mixed with PEDOT: PSS were reported as having suitable properties for supercapacitors, in which SWCNTs can increase specific capacitance by 65 % compared with pristine PEDOT: PSS [13]. Moreover, multiwalled carbon nanotubes (MWCNTs) mixed with PEDOT: PSS (MWCNTs/ PEDOT: PSS) were also studied, and it was found that the mixture provided high specific capacitance, and PEDOT: PSS could also maintain the specific capacitance [10].

In this work, a flexible electrode, MWNCTs/PEDOT: PSS coated on pineapple fiber paper, was developed. The electrical conductivity of MWNCTs/PEDOT: PSS was evaluated as a function of MWCNT concentration. Then, the optimized MWNCTs/PEDOT: PSS was coated on pineapple fiber paper and investigated for electrochemical applications.

2. Materials and Methods

The pineapple fiber paper was used as a substrate of green flexible electrodes. The active material, MWNCTs/PEDOT: PSS, was coated on pineapple fiber paper. The details of electrode preparation and characterization are described as follows.

2.1 Electrode preparation

2.1.1 Preparation of MWCNTs/PEDOT: PSS

MWCNTs/PEDOT: PSS was prepared according to previous work [14]. Firstly, 1 g PEDOT: PSS (dry, Sigma-Aldrich) was dissolved in 4 g dimethyl sulfoxide (DMSO) (Sigma-Aldrich, 99.9 %,).

The control was 1:4 w/w. MWCNTs (12 nm diameter, 3-12 µm length, and purity >95 wt%) were purchased from Nano Generation Co., Ltd. The 0.5, 1, 2, 3, and 5% wt. MWCNTs were mixed with PEDOT: PSS at room temperature.

2.1.2 Preparation of fiber paper flexible electrode

Commercial pineapple fiber paper 100% from a community enterprise in Ratchaburi province, Thailand was used as the paper electrode supporter. The PEDOT: PSS and MWCNTs suspensions in various concentrations of MWCNTs were spread onto the pineapple fiber papers. A 0.1 g sample of suspension was dropped onto a 1 cm^2 pineapple fiber paper. The suspension was spread by the doctor blade method and dried at room temperature in a desiccator.

2.2 Characterizations

The morphologies of MWCNTs/PEDOT: PSS coated on pineapple fibers papers were observed by scanning electron microscopy (SEM) and compared to uncoated paper. The semicrystalline polymer was characterized by FTIR (Fourier Transform Infrared) spectroscopy.

2.2.1 Electrical conductivity measurement

Electrical conductivity of the electrode was measured by four point probe resistivity measurement. The electrical conductivity was calculated from the relation described in equation (1)

$$\sigma = \frac{l}{RS} \tag{1}$$

where σ is the electrical conductivity (S cm^{-1}), R is the electrical resistance (Ω), S is the cross-sectional area of the fiber (cm^2), and l is the length of the test fiber (cm) [15]. The cross-section area of fiber was measured by microscope camera.

2.2.2 Electrochemical measurements

The electrochemical performance was evaluated by cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) in the frequency range of 10 mHz to 100 kHz. All techniques were carried out by µAutolabIII with three-electrode system. The three-electrode system was composed of Ag/AgCl as reference electrode, a platinum rod as counter electrode and the fiber paper flexible electrode as working electrode. The electrolyte solution was 1 M lithium chloride solution (LiCl). The electrode potential was cycled in the potential range of -0.9 to -0.2 V with a scan rate of 50 mV s^{-1}.

3. Results and Discussion

SEM images of pineapple fiber paper samples are shown in Figure 1(a and b). The mean diameter of fibers is in the range of nanometers to 10 µm. Figure 1(b) is a zoom in picture (20 times) and shows that the surface of the pineapple fiber was quite rough. The fiber surface helps easy adhesion. It can be clearly seen that MWCNTs/PEDOT: PSS was well distributed and covered onto the pineapple fiber paper, as shown in Figure 1(c). In Figure 1(d), MWCNTs/PEDOT: PSS was obviously fixed between the fiber cross-link networks. MWCNTs as shown in Figure 1(d)

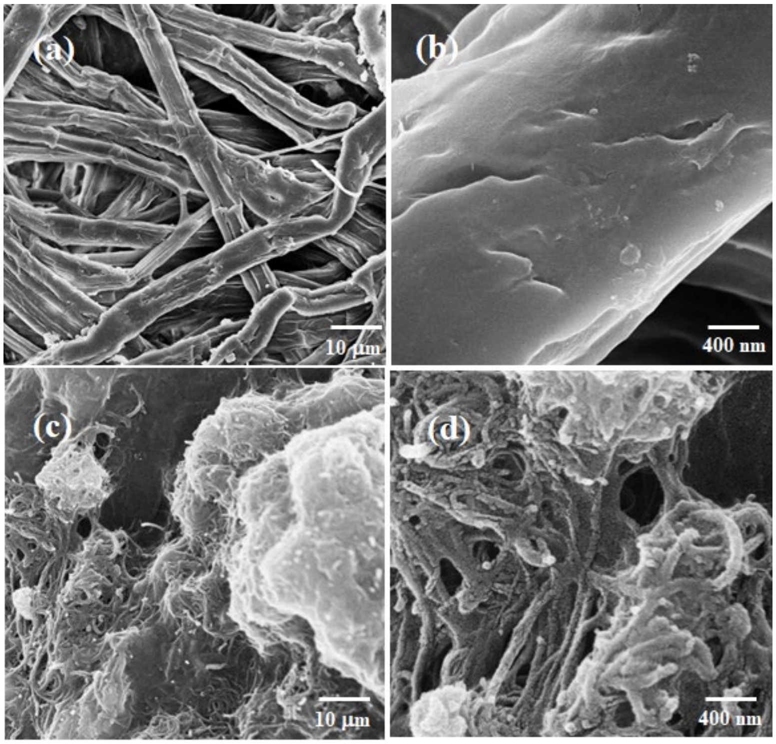

Figure 1. (a and b) Morphology of pineapple fiber paper and (c and d) MWCNTs/PEDOT: PSS coated on fiber paper

demonstrated a good spread due to Poly (styrene sulfonate) (PSS). The diameter of MWCNTs is less than 50 nm.

Figure 2 shows the FTIR spectra of pineapple fiber paper, MWCNTs, PEDOT: PSS and MWCNTs/PEDOT: PSS coated on fiber paper. The absorption bands of MWCNTs at 1384 cm^{-1} and 1634 cm^{-1} indicate C-C and C=C stretching of CNT and CNT backbones, respectively [16, 17]. The vibration at 1171 cm^{-1} and 1147 cm^{-1} of PEDOT: PSS point to the sulfonate group of PSS [18, 19]. The cellulose wave number is at 1050 cm^{-1}, which corresponds to previous work [20]. The FTIR spectra shows that all peaks appearing in pineapple fiber paper, MWCNTs and PEDOT: PSS can be found in MWCNTs/PEDOT: PSS coated on fiber paper.

The electrical conductivity of the paper electrode coated with MWCNTs/ PEDOT: PSS composite was studied. The electrical conductivity was measured as a function of MWCNT concentration. The result is shown in Figure 3. The addition of MWCNTs to the PEDOT: PSS on the fiber paper increased conductivity from 0.112 to 10.87 S cm^{-1}. This effect of MWCNTs on electrical conductivity is in good agreement with previous work [14]. This is because MWCNTs are typical conjugated polyene structures that permit easy electron movement. As shown in Figure 3, the 3% MWCNTs/PEDOT: PSS was the condition at which the highest electrical conductivity was displayed while 5% MWCNTs shows decreased electrical conductivity because charge carriers had too much path way selection. Under this condition, they will select a path in gain boundaries, resulting in decreased charge mobility and also decreased electrical conductivity [21].

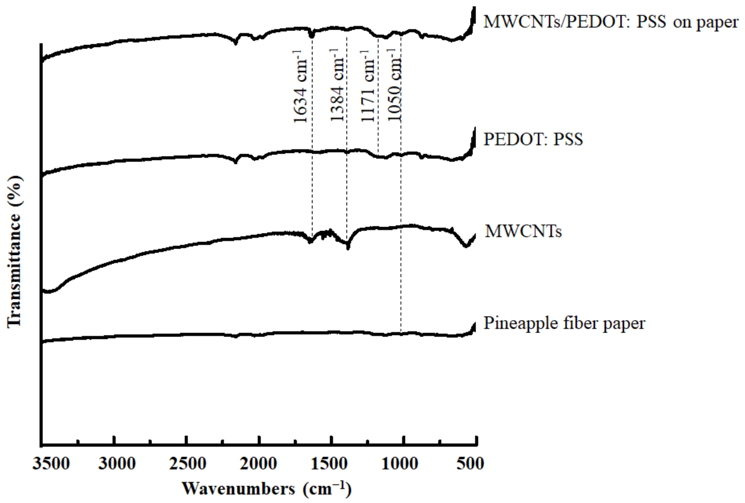

Figure 2. FTIR spectra of pineapple fiber paper, MWCNTs, PEDOT: PSS and MWCNTs/PEDOT: PSS coated on fiber paper

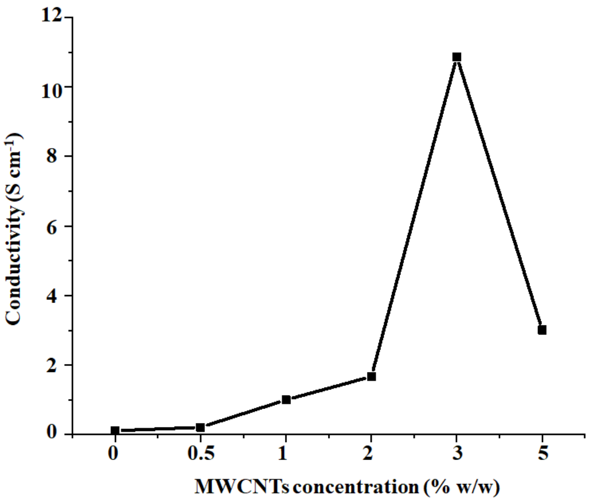

Figure 3. Conductivity of MWCNTs/PEDOT: PSS on paper as a function of MWCNT content

The cyclic voltammograms of the fiber electrode coated with 3%MWCNTs/ PEDOT: PSS and of the fiber electrode coated by pristine PEDOT: PSS for comparison were plotted and are shown in Figure 4. The electrical current response of pristine PEDOT: PSS appears to be close to zero. The CV curve indicated that pristine PEDOT: PSS may have low electrical conductivity due to the insulating of PSS [22]. The electrical current response of 3% MWCNTs/PEDOT: PSS coated paper is higher than that of pristine PEDOT: PSS coated paper due to its higher electrical conductivity [23]. The CV curve implied that the capacitive performance of an electrode that can be determined from the area under the curve [24]. From the area under the CV curve, a specific capacitance (C_p) can be calculated using equation (2) [25, 26], and it was found that the specific capacitance of 3% MWCNTs/PEDOT: PSS coated on fiber paper electrode equaled 0.011 Fg^{-1}. This indicated that charges could be stored at the surface of the fiber electrode (MWCNTs/PEDOT: PSS coated on fiber paper), allowing the use of the fiber electrode in electrochemical storage devices. However, the CV curve shows deviation from the rectangular shape suggesting the presence of faradaic process at the interface between electrode and electrolyte solution.

$$C_p = \frac{area\ under\ the\ curve}{mass\ of\ electrode \times scan\ rate \times voltage} \qquad (2)$$

The CV curves of 3%MWCNTs/PEDOT: PSS at various scan rates are shown in Figure 4(b). The current density (i) can be calculated using equation 3 [15, 25], which shows the relation between current density and specific capacitance. The current densities of the electrode at scan rates of 10, 20, and 50 mV s^{-1} were 0.35, 0.44, and 0.55 mAg^{-1}, respectively. The electrode current was directly proportional to the scan rate, indicating that the rate performance of 3%MWCNTs/PEDOT: PSS was acceptable.

$$current\ density\ (i) \ = \ C_p \times scan\ rate \qquad (3)$$

where C_p is specific capacitance (Fg^{-1}).

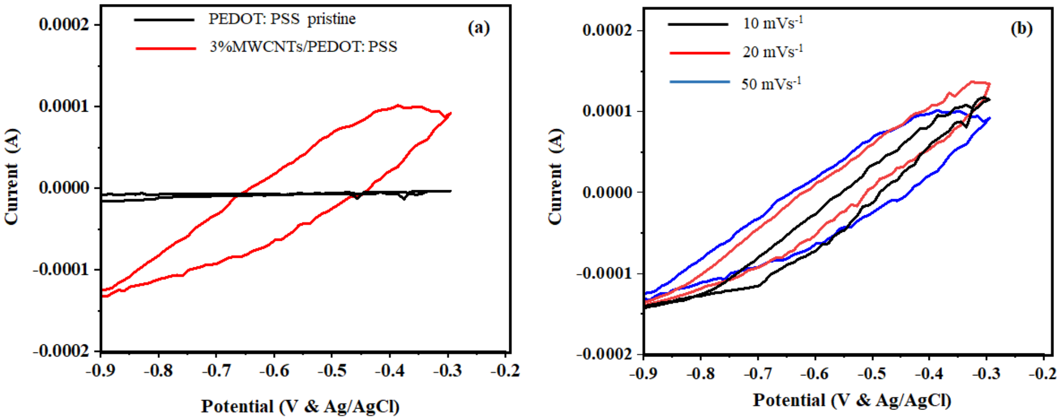

Figure 4. Cyclic voltammograms of (a) pineapple fiber electrode that coated by pristine PEDOT: PSS and 3%MWCNTs/PEDOT: PSS at scan rate of 50 mVs^{-1} and (b) 3%MWCNTs/PEDOT: PSS at various scan rates

To investigate the impedance of the electrode, EIS measurement in the frequency range of 0.01 Hz to 100 kHz was performed. The EIS spectra of fiber electrode coated with pristine PEDOT: PSS and 3%MWCNTs/PEDOT: PSS are displayed in Figure 5. From the spectra, series resistance (R_s) can be calculated from the distance between $-Z''$ axis and origin point of spectra. The series resistance indicates the internal resistance of an electrode material and electrolyte solution. The series resistances of pristine PEDOT: PSS and 3%MWCNTs/PEDOT: PSS were different (149.9 and 130 **Ω**, respectively). Although the resistivity was too high, the Nyquist plots showed the possibility of developing this material into an energy storage electrode.

The Nyquist plot is composed of a semicircle at high/medium frequency range and a straight inclined line at a low-frequency range. The semicircle indicates charge transfer resistance at the interface between electrode and electrolyte. Charge transfer resistance refers to charge transfer by an electrochemical reaction that depends on reaction kinetics. The other part, the straight inclined line at a low-frequency range, correlates to the diffusion of electroactive species into electrode materials (Warburg resistance, W) [27]. The EIS spectra of PEDOT: PSS electrode displayed a straight inclined line. This suggests that ion diffusion between the interface of electrode surface and electrolyte is the main mode of the electrode [26, 28]. The semicircular part of the EIS spectrum of 3% MWCNTs/PEDOT: PSS electrode illustrates charge transfer resistance. This indicates that 3% MWCNTs/PEDOT: PSS electrode has electronic and ionic conductivities while the pristine PEDOT: PSS has only ionic conductivity. These electronic and ionic conductivities are beneficial for redox reactions in an electrode/electrolyte system.

From the diameter of semicircle, charge transfer resistance was calculated and equaled 433.89 Ω which was quite low compared with MWCNTs/cellulose paper electrode, which provided charge transfer resistance of 580 Ω [29]. An acceptable electrochemical electrode for energy storage should have both high diffusion process and optimum kinetic process [30]. The MWCNTs/PEDOT: PSS system can be used as an energy storage device because it has both kinetic process and diffusion process. Moreover, the results of the CV and EIS analysis suggest that MWCNTs can improve the electrode properties, electrical conductivity and specific capacitance although the specific capacitance of MWCNTs/PEDOT: PSS sample was lower than that reported in previous research [9]. However, the good conductivity of the MWCNTs/PEDOT: PSS electrode is supportive to the improvement of its capacitive behavior. It can be improved by decreasing the ohmic contact between electrode and electrical wire and further developing the electrode fabrication method. One possibility is to coat MWCNTs onto the pineapple fibers before forming the paper. Moreover, the electrical capacitance properties can be increased by adding a metal oxide to increase the catching ions.

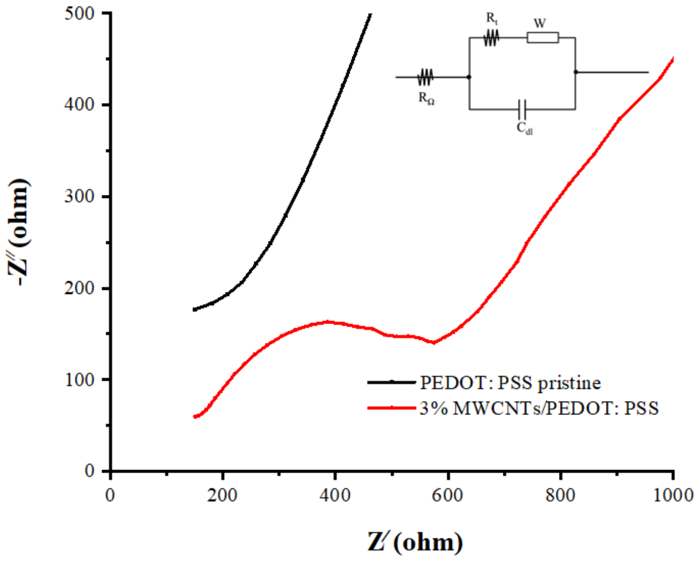

Figure 5. Impedance curve of pineapple fiber paper electrode that coated by pristine PEDOT: PSS and 3%MWCNTs/PEDOT: PSS

4. Conclusions

MWCNT/PEDOT: PSS coated on pineapple fiber paper can be applied as an electrode for electrochemical storage devices. 3%MWCNTs/PEDOT: PSS proved to be the combination providing the highest electrical conductivity and specific capacitance, which were 10.87 Scm^{-1} and 0.011 Fg^{-1}, respectively. The 3%MWCNTs/PEDOT: PSS electrode has the characteristics of a capacitor and is a good candidate for developing into an environmentally friendly flexible electrode. To improve specific capacitance value, its electrical conductivity and diffusion process can be enhanced further by adding metal oxide.

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