Journal of Physics: Conference Series

PAPER • OPEN ACCESS

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Journal of Physics: Conference Series **1835** (2021) 012106 doi:10.1088/1742-6596/1835/1/012106

Effect of acid treatment substrate for supercapacitor electrode based on multi-walled carbon nanotubes

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Abstract. Effect of acid treatment substrate for supercapacitor based on multi-walled carbon nanotubes (MWNTs) electrode was investigated. The electrode was used as stainless steel type 304 (SS304) and was with hydrochloric acid (HCl) acid-treated before use. Firstly, SS304 substrates were soaked in 37% HCl for designated time. Acid treatment times were varied at 0, 5, 10 and 15 min. Their surface morphology, elemental components and hydrophilicity property of the acid-treated SS304 were analyzed. The 10-min-treated SS304 show the lowest contact angles, indicating the best hydrophilicity property. Electrode material was prepared by composites of MWNTs, polyvinylidene fluoride (PVDF) and n-methyl-2-pyrrolidone (NMP) with an area of 5x5 mm^2. Their cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) were characterized. The 10-min-treated SS304 exhibits the best performance with a specific capacitance (SC) of 261.04 Fg^{-1}. The improvement of the SC of the acid-treated substrate was contributed to the adhesion improvement between a current collector and an electrode material, and the hydrophilicity improvement, resulting in a large amount of electrolyte ions accessing into the electrode materials and subsequently enhancement of their capacitive characteristics.

1. Introduction

Currently, there are discovered in renewable production from the sun, wind and water, as well as the improvement of electronic devices. Supercapacitor have come to called an electrochemical capacitor, is a combine between high power capability and good specific energy bridging the gap between batteries and conventional capacitors. Supercapacitors exhibit a higher power density than battery, a higher energy density than conventional capacitors, very fast charging, and long cycle life [1-5]. Supercapacitors are separated with charge storage mechanisms such as pseudocapacitors, electrical double-layer capacitors (EDLCs) and Asymmetric supercapacitors (ASCs) [3]. For supercapacitor, the carbon nanomaterials are the most generally used as electrode materials for EDLCs because of high surface area, good conductivity, and good electrolyte accessibility [6]. For pseudocapacitors, electrode materials were used as transition metal oxide and conducting polymer [7]

The structure of supercapacitor consists of electrodes, separator, and electrolyte. To enhancement of supercapacitor, the most commonly focused on the improvement of current collector or electrode materials. The current collector can be used as low resistivity and excellent hydrophilic property for the easies electrolyte ions accessing into the electrode materials and subsequently enhancement of their capacitive characteristics. In this work, we study on the effect of acid-treated SS304 substrate and electrochemical properties for supercapacitor based on multi-walled carbon nanotubes (MWNTs) electrode.

2. Experimental method

Stainless steel type 304 (SS304) was adopted as electrode substrate and was acid-treated before use. SS304 substrates were soaked in 37% hydrochloric acid (HCl) for designated time and washed with deionized (DI) water to remove residual HCl solution. Acid treatment times were varied at 5, 10 and 15 min. The MWNTs paste was prepared by the procedure described elsewhere [8] and coated on the treated-SS304 with an area of 5x5 mm^2. Firstly, MWNTs were thermal-treated at 500°C for 1 h and were microwave-treated at 650 W for 70s. Then, the electrode solution was mixed with the treated MWNTs and PVDF at the weight ratio of 11:1 in NMP. The treated-SS304 substrates were characterized by field-emission scanning electron microscopy (FE-SEM; HITACHI-S4700), energy dispersive x-ray spectroscopy (EDX; iXRF system SphinX 130) and contact angle technique (Dataphysics OCA 40).

For device assembly, a filter membrane (PTFE, Millipore) was inserted between a pair of MWNT-coated SS304 and 1 M H_2SO_4 was used as an electrolyte. For supercapacitor performance characterization, cyclic voltammetry (CV), galvanostatic charge/discharge (CD) and electrochemical impedance spectroscopy (EIS) were measured using an electrochemical workstation system (Metrohm Autolab Potentiostats & Galvanostats,). CV test and CD test were measured of voltage range between 0.0 to 0.8 V at scan rates of 100 mVs^{-1} and between 0.0 to 1.0 V at a current of 1 mA, respectively. EIS was measured at a frequency range between 10 kHz to 0.01 Hz at an amplitude of 5 mV. The specific capacitances of supercapacitor were calculated by the following equations;

$$C_{sp} = \frac{\int_{V_2}^{V_1} i(V)dV}{2(V_2 - V_1)mv} \tag{1}$$

where $\int_{V_2}^{V_1} i(V)dV$ is total voltammetric charge of positive and negative sweep in CV curve, V_2-V_1 is voltage window width (V), m is a weight of carbon nanomaterials in the electrode paste (g), v is a scan rate (Vs^{-1}).

3. Results and discussion

Morphology

The morphological structure of the acid-treated SS304 substrate are shown in Figure 1, while table 1 corresponding to their element evaluation by EDX. Fig 1(a) show an untreated SS304 substrate. Figure 1(b)-1(d) shows the acid-treated SS304 substrates for 5, 10 and 15 min, respectively. After acid-treatment SS304 substrate, the surfaces become rougher. The passivation of SS304 would be

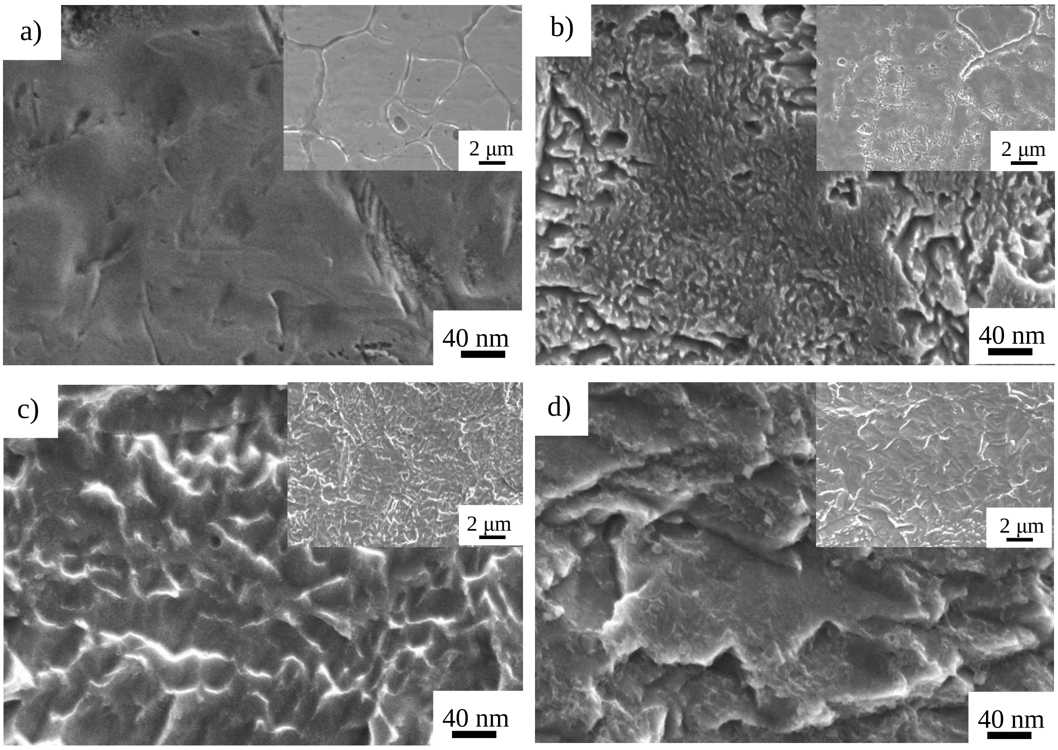

Figure 1. FE-SEM images show the morphological structure of acid-treatedSS 304 substrates (a) 0 min; (b) 5 min; (c) 10 min and (d) 15 min

complete by deposition and coverage of chromium-rich oxide layer and trivalent iron oxide which is derived from oxidation of divalent iron [9]. It is well know that the exceptional corrosion of stainless steels is caused by passive chromium oxide film formed on the surface. After treatment, HCl transports into the passive film. Then, the passive film is attacked or dissolved. And finally, the passive film is removed by undercutting. The surface is rough because HCl behavior is non-uniform dissolution. Table 1 shows elemental evaluation of SS304 at different treatment times determined by EDS measurement. An untreated SS304 substrate consists of carbon, oxygen, chromium, iron and nickel in concentration of 0.11±0.08, 1.42±0.22, 15.00 ±2.93, 74.36±1.24, and 9.10±4.03 wt%, respectively. The EDS results confirm the passive chromium oxide film formation on the surface. The 5-min-treated SS304 substrate consists of carbon, oxygen, chromium, iron and nickel in concentration of 0.54±0.16, 0.83±0.13, 15.26 ±1.00, 72.04±0.58, and11.34±1.55 wt%, respectively. The EDS results confirm the decrease of oxygen concentration; imply that passive chromium oxide film had exfoliated. The 10-min and 15-min treated SS304 substrate consists of carbon, oxygen, chromium, iron and nickel in concentration of 0.67±0.47 and

Table 1 Element evaluation using Energy Dispersive Spectroscopy (EDS)

Element	Concentration (wt%)			
	0 min	5 min	10 min	15 min
Carbon	0.11±0.08	0.54±0.16	0.67±0.47	0.76±0.16
Oxygen	1.42±0.22	0.83±0.13	1.06±0.13	1.22±0.07
Chromium	15.00±2.93	15.26±1.00	16.25±2.34	15.98±1.38
Iron	74.36±1.24	72.04±0.58	73.04±3.32	72.12±1.53
Nickel	9.10±4.03	11.34±1.55	8.99±1.32	9.92±3.06

0.76±0.16, 1.06±0.13 and 1.22±0.07, 16.25±2.34 and 15.98±1.38, 73.04±3.32 and 72.12±1.53, 8.99±1.32 and 9.92±3.06 wt%, respectively. The EDS confirm the increase of oxygen concentration, indicates that the surface of SS304 substrate has passive chromium oxide film again.

The contact angle measurement was conducted to test the surface substrate wettability. The hydrophobic property is showed contact angle (CA) greater than 90° whereas the CA is smaller than 90°, indicating hydrophilic property [10]. Figure 2 shows the shape of 1 M H_2SO_4 droplet on the surface of SS304 substrates at different treatment times. The CA of treatment times; 0, 5, 10 and 15 min for droplet before dip-coated on SS304 substrate are about 60.99±3.67, 40.38±9.11, 13.02 ±1.59, and 13.54±1.00 degree, respectively. On the other hand, the CA of treatment times 0, 5, 10 and 15 min for droplet after dip-coated on SS304 substrate are about 113.92±1.52, 104.11±1.95, 14.98 ±4.42, and 16.99±4.52 degree, respectively. It is well know that the increase of degree after MWNT coated onSS304 substrate is caused by MWNT are hydrophobic materials due to sp^2 lattice of graphitic carbon. This results indicates that 10 min-tratment on SS304 substrate show the low contact angles, leading to improved surface wettability of the 10 min-treated by 37% HCl acid have hydrophilic properties. The hydrophilicity improvement, resulting in a large amount of electrolyte ions accessing into the electrode materials and subsequently enhancement of their capacitive characteristics that is one of the prime requirement for enhancement performance of supercapacitor[11].

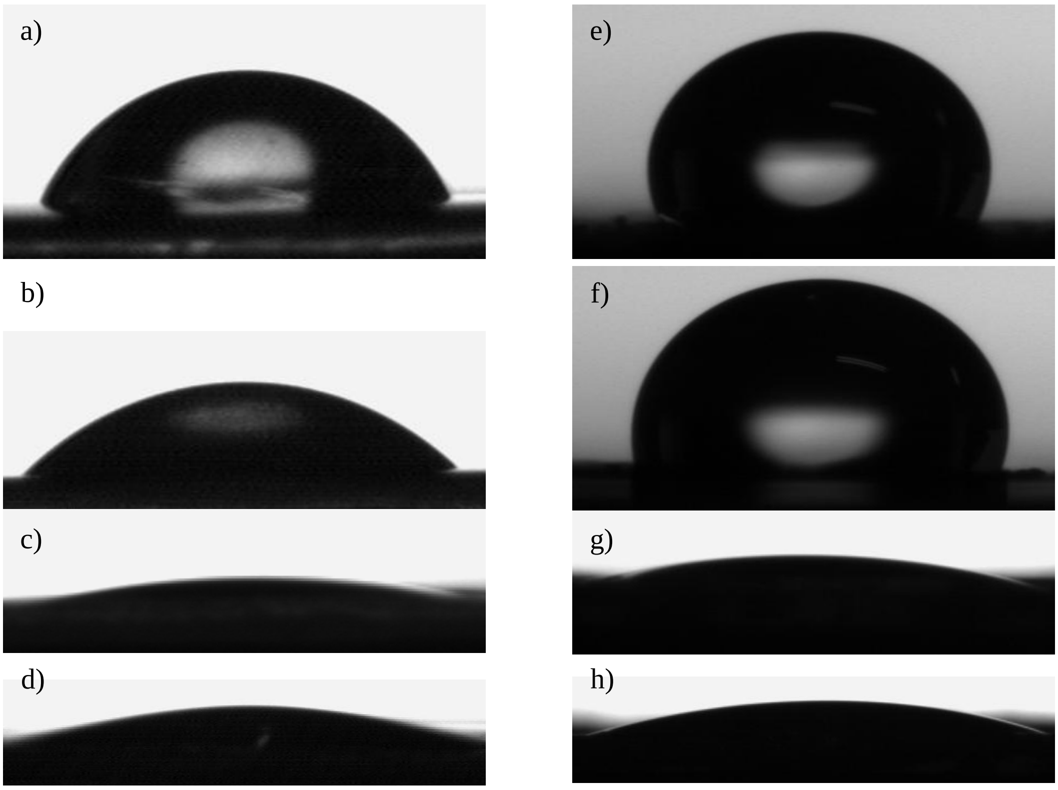

Figure 2. Contact angles of electrolyte droplet on acid-treated SS304 and MWNTs-coated-acid-treated SS304 substrates at the acid treatment time of (a),(e) 0, (b),(f) 5, (c),(g) 10 and (d),(h) 15 min, respectively.

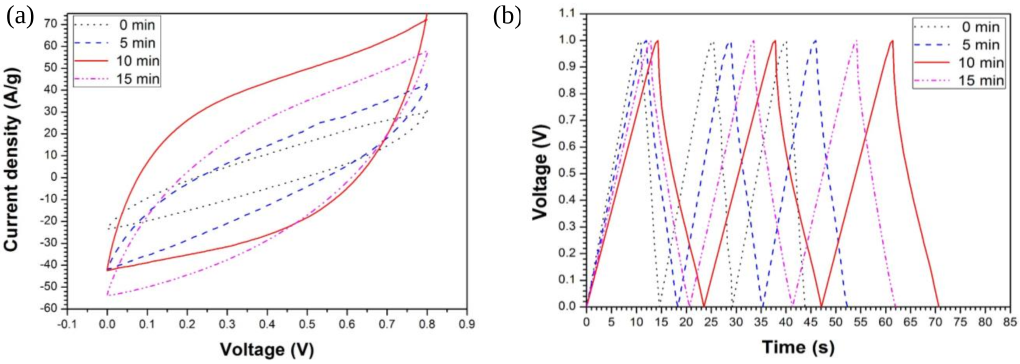

Figure 3. (a) Cyclic voltammograms of different condition of acid treatment at scan rate of 1 00 mVs^{-1}; (b) galvanostatic charge/discharge curves of different condition of acid treatment at an applied constant current of 1 mA.

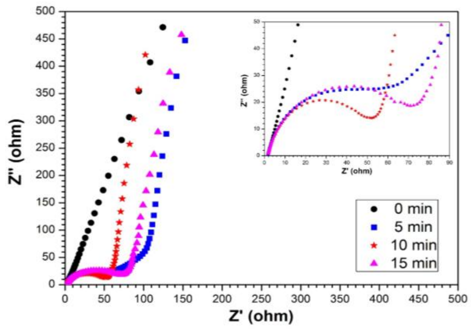

Figure 4. Nyquist plot of different condition of acid treatment in the frequency range of 10 kHz – 0.01 Hz for amplitude 5 mV

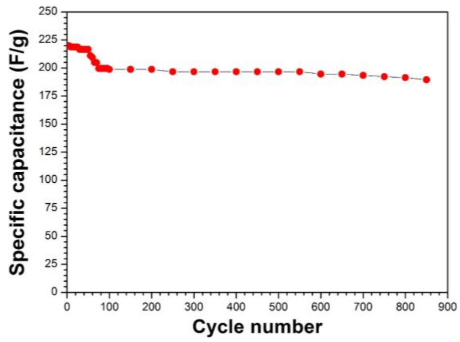

Figure 5. Charging/discharging cycling stability of 10 min-treatments on SS 304

Figure 3(a) shows CV curves of 0, 5, 10 and 15 min acid-treated SS 304 substrates in a voltage range between 0 to 0.8 V at a scan rate of 100 $mV{\cdot}s^{-1}$. The CV curves showed qusi-rectangular shape with typical EDLC. The specific capacitances were calculated using Eq. (1) by the area of CV curve. The specified capacitances of 0, 5, 10 and 15 min acid-treated SS 304 substrates were 153.52, 177.61, 261.04 and 210.49 $F{\cdot}g^{-1}$, respectively. The 10 min-treated show the best of specific capacitance. Figure 3(b) shows the galvanostatic charge-discharge (CD) curves of different condition of acid treatment at an current of 1 mA. The CD showed a shape of a similarly triangle, implying good electrochemical reversibility and a small voltage drop, indicating a low internal resistance of the electrode [12]. The electrochemical impedance spectroscopy (EIS) can be explained the resistance and capacitance of supercapacitor electrode. Figure 4 shows the Nyquist plots of different condition of acid treatment in the frequency range between 10 kHz – 0.01 Hz for amplitude 5 mV. The Nyquist spectra consists of two regain part. The parts of high frequency region show a semicircle whereas a linear portion extending in the low-frequency regions. The 10-min and 15-min shows a straight line with a slope near unity, implying in a large amount of electrolyte ions accessing into the electrode materials, and suggesting an ideal supercapacitive behavior. The resistance of supercapacitor electrode consists of intrinsic resistance of the electrode material, electrolyte resistance and contact resistance between the current collector and electrode materials, which is called series resistance, R_S [13]. The R_S values of the 0, 5, 10 and 15 min-acid treated SS 304 substrates are determined to be 1.82, 1.84, 1.66 and 1.90 Ω, respectively. 1 M H_2SO_4 electrolyte was used in the EIS measurement, a decrease in the R_S of the 10-min treated SS304 substrate may be attributed to a decrease in contact between the current collector and electrode materials due to the improvement of the hydrophilic property. Figure 5 shows the specific performance of 10 min-acid treated SS304 substrate. The specific capacitance remains 86% after 850 cycles. This result shows good stability with good retention of capacitance and will be use as energy storage devices.

4. Conclusion

Supercapacitor based on multi-walled carbon nanotubes using 10 min-acid treated SS304 substrate was successfully fabricated. Acid-treated SS304 show the hydrophilicity improvement and large amount of electrolyte ions accessing into the electrode materials and subsequently enhancement of their capacitive characteristics.These preliminary results suggest that the 10 min-acid treated SS304 substrate will be use as electrode material for EDLC application.

Acknowledgment

We acknowledge the support from the KMITL Research Fund (KREF045508) and support from the National Nanotechnology Center (NANOTEC), NSTDA, Ministry of Science and Technology, Thailand, through its program of the Center of Excellence Network and the Thailand Center of Excellence in Physics (ThEP). P.D. acknowledges the support from the Thailand Research Fund (TRF). We thank Thai Microelectronics Center (TMEC), National Electronics and Computer Technology Center (NECTEC) for FE-SEM observation.

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