

Electrochemical performance of activated carbon and graphene based supercapacitor

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A conventional but simple fabrication technique of activated carbon/graphene (AC/G) supercapacitor electrode will be presented in this work. The AC/G electrode was prepared using slurry technique from the mixture of AC and graphene powders, polytetrafluoroethylene as binder and *N*-methylpyrrolidone as solvent. The AC/G electrode was dried at 120°C in vacuum oven for 6 h followed by immersing in 1M lithium hexafluorophosphate electrolyte for another 6 h. The specific gravimetric capacitance of the electrode was calculated to be 19.45 F g⁻¹ using cyclic voltammetry at a scan rate of 1 mV s⁻¹. Electrochemical behaviour including charge discharge and impedance characteristics confirmed the electrode's ability as a possible active material for use in carbon based supercapacitor.

Keywords: Activated carbon and graphene electrode, Supercapacitor, Slurry technique, LiPF₆ electrolyte, Electrochemical analyses

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Introduction

An increasing demand for energy system and climate change has made a high concern in research on the development of advanced energy storage devices.¹ Generally, energy storage devices such as batteries, fuel cells and supercapacitors are being used to store energy for various applications including mobile phones, laptops, airplanes, buses, hybrid electric vehicles, etc.² Recently, supercapacitors are considered as one of the most promising energy storage devices due to its high rate performance, such as long life cycle and outstanding power density.³

Basically, supercapacitor can be classified into two types according to the mechanism of energy storage, which are electrochemical double layer capacitors (EDLCs) and pseudocapacitors. The capacitance of EDLCs charges is separated across the interface between electrode and electrolyte, with high surface area materials. By contrast, pseudocapacitors arise from fast and reversible redox reactions of electroactive materials with several oxidation states (metal oxides and conducting polymers).⁴

There are few types of carbon based that are normally used as electrode materials in EDLC. The usage of these carbons as electrode is because the performance of supercapacitor is strongly dependent on the properties of electrodes. Various carbon materials including activated carbon, carbon aerogels, mesoporous carbon, carbon onions and carbon nanotubes are the most commonly used materials as electrodes due to their

ability of having higher surface area and to produce capacitors with an enhanced specific capacitance. Apart from that, these carbonaceous materials are chemically and thermally stable and environmentally friendly.⁵ Graphene is an extraordinary allotrope of carbon, a single atom thick with a single layer of two-dimensional nanostructure of sp² bonded carbon material,⁶ owing to its high aspect ratio, excellent electrical conductivity and good mechanical properties.⁷

Herein, we report a low cost and scalable approach for the preparation of supercapacitor electrode fabrication using conventional slurry technique. The charge storage properties of the supercapacitor were then evaluated by various electrochemical measurements.

Experimental

Preparation of AC/G electrode

For the AC/G slurry, commercially available activated carbon powder with specific surface area (SSA) of 1800 m² g⁻¹ (RP20; Kuraray), graphene powder with SSA of 120–150 m² g⁻¹ and polytetrafluoroethylene were used in the weight ratio of 55 : 40 : 5. These materials were mixed together with *N*-methyl pyrrolidone solvent. The resulting mixture was coated onto stainless steel mesh and pressed to 6000 Psi using hydraulic hand press. The pressed electrode was then dried at 120°C in vacuum oven for 6 h time. It was followed by immersing in the electrodes in the LiPF₆ electrolyte for another 6 h time in glove box. The electrode was then ready for supercapacitor cell assembly before electrochemical testing. Listed in Table 1 below is the important items/materials needed to fabricate the electrodes.

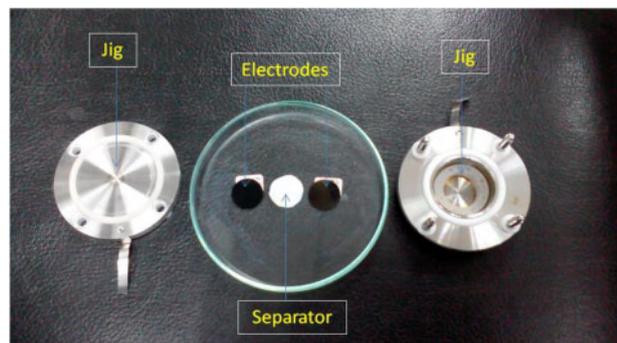
Electrochemical measurements

The supercapacitor was constructed with two AC/G symmetric electrodes separated by 25 μm polypropylene (Tonen) as separator, and 1M LiPF₆ solution as

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1 Digital image of AC/G supercapacitor components before assembly process

electrolyte. AC/G supercapacitor was assembled using a battery jig (Takumi Giken) according to the order shown in Fig. 1. All electrochemical measurements were carried out at room temperature (25°C).

Cyclic voltammetry (CV) and galvanostatic charge discharge measurements were performed using potentiostat/galvanostat (Wonatech: WBCS3000). Cyclic voltammetry measurement was conducted to measure the cyclic behaviour of the electrode and also to determine their specific gravimetric capacitance C_{sp} . The applied voltage was set to 0.0 to 3.5 V due to the organic electrolyte's thermodynamic window, which can be up to 5.0 V. The scan rate was set to 1, 5, 10, 50 and 100 mV s^{-1} . In addition, charge discharge measurements were conducted to measure the charging and discharging time of electrode with the different applied currents, namely 10, 13, 15 and 17 mA. The electrochemical impedance spectroscopy measurement was then conducted using frequency response analyser (Metrohm Autolab). Electrochemical impedance spectroscopy measurement was carried out with the frequency range from 100 KHz to 0.1 Hz at the amplitude of 10 mV.

Results and discussion

Cyclic voltammetry

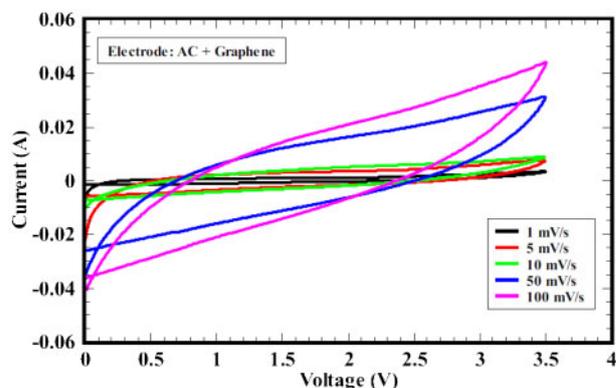
Capacitive behaviour of the AC/G electrode was determined using CV because this method provides valuable information on the charge discharge behaviour of the electrodes. At 1 mV s^{-1} of CV scan rate, the C_{sp} was calculated to be 19.45 F g^{-1} . To observe such supercapacitor behaviour over a range of scan rate, Fig. 2 shows the CVs for the AC/G electrode at five different scan rates (1, 5, 10, 50 and 100 mV s^{-1}). It demonstrates that the current response increased with the scan rates. The C_{sp} of the AC/G electrode was calculated using equation (1) from the CVs recorded with a scan rate of 1, 5, 10, 50 and 100 mV s^{-1}

$$C_{sp} = \int_{E_1}^{E_2} i(E) dE \div 2(E_2 - E_1)mv \quad (1)$$

where E_1 and E_2 are the cutoff potentials in CV. $i(E)$ is the current. $\int_{E_1}^{E_2} i(E) dE$ is the total voltammetric charges

Table 1 Cell construction of AC/G supercapacitor

Current collector	15 mm diameter of SS mesh
Active material	Activated carbon and graphene powders
Binder	Polytetrafluoroethylene
Electrolyte	Organic electrolyte 1M LiPF ₆
Separator	Polypropylene



2 Cyclic voltammetry curves of AC/G electrode measured at various scan rates (1, 5, 10, 50 and 100 mV s^{-1})

obtained by integration of positive (charge) and negative (discharge) sweeps in CV. $(E_2 - E_1)$ is the cell potential window width. m is AC/G mass per electrode, and v is the scan rate.

The low C_{sp} value is not only because of the originally low SSA of the graphene but could also possibly due to the poor ion accessibility in the AC/G pores. If the pore size of the material is smaller than the electrolyte's ions, then sieving effect will not occur. Owing to this phenomenon, the usage of the carbon surface area is underused.⁹ In addition, poor attachment structure between AC and graphene can also be the reason for the low capacitance performance.

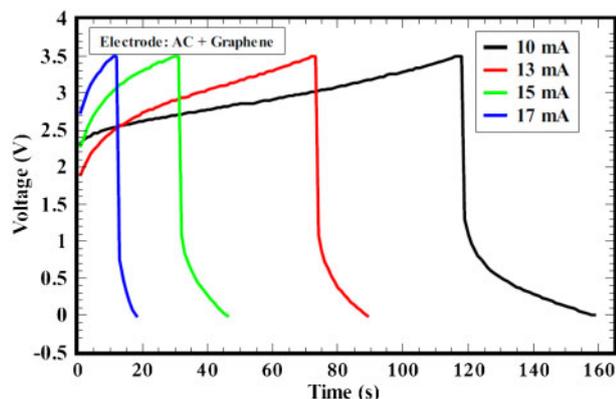
Furthermore, as the scan rate increased $>5 \text{ mV s}^{-1}$, the CV 'window' tended to tilt toward the vertical axis, thereby becoming a quasi-rectangle. This result indicates the dominance of the double layer formation in the energy storage process at lower scan rates. It is also observed that the CVs for all scan rates in Fig. 2 do not have any redox peaks, indicating that the supercapacitor is free from chemical reactions and/or is purely based on the electrostatic (physical separation) mechanism.¹⁰

Galvanostatic charge discharge

The charge storage ability of AC/G supercapacitor in 1M LiPF₆ was further evaluated by galvanostatic charge discharge test performed at different currents, 10, 13, 15 and 17 mA, with fixed voltage swept from 0.0 to 3.5 V and back to 0.0 V (Fig. 3). It was continuously measured up to (but not limited to) 10 cycles. In addition, the supercapacitor operated at very rapid charge discharge performance (in seconds) and which is a well known advantage for supercapacitor. The various constant currents were applied to observe the ability of the electrode to work from lower to higher current density. From the charge discharge curves, the C_{sp} of the supercapacitor can be calculated by³

$$C_{sp} = \frac{2I}{m \left(\frac{dV}{dt} \right)} \quad (2)$$

where I is the applied current, m is the mass of the active material in each electrode and dV/dt is the slope of the discharge curve after the Voltage (IR-) drop. The charge discharge curves of AC/G electrode depict that the C_{sp} decreased with increasing applied currents, from 9.2 F g^{-1} at 10 mA to 0.52, 0.51 and 0.26 F g^{-1} at 13, 15 and 17 mA respectively.



3 Galvanostatic charge discharge curves for AC/G electrode at different applied currents (10, 13, 15 and 17 mA)

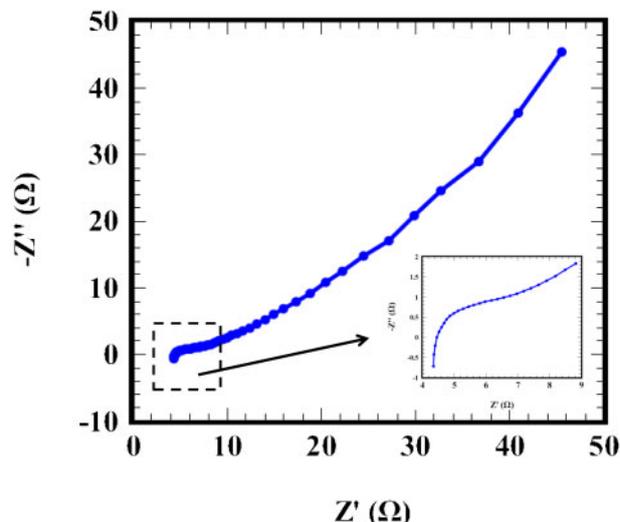
From charge discharge, the shape of curve is not nearly triangular because of the large internal resistance or equivalent series resistance (ESR) that causes a large ohmic drop at high discharging electrode. On the other hand, large ESR causes a large ohmic drop at high discharging current, resulting in the decrease in the specific capacitance.¹¹ Polytetrafluoroethylene binder material used is less conductive, which may become barriers in the access paths for electrons and electrolyte ions, and thus increase the internal resistance.¹²

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy has been used to investigate the resistivity performance of supercapacitor, for example the charge transfer and electrolyte resistance. Figure 4 shows the relation between Z'' (imaginary) and Z' (real) impedance curve for AC/G electrode measured in a 1M LiPF₆ electrolyte. Generally, by analysing the electrochemical impedance spectroscopy spectrum in the high frequency region, one can measure the ESR of the electrode, which equal to the sum of various resistance contributions, such as the inherent resistance of the electrode materials (including the active material and current collector), the bulk resistance of the electrolyte and the contact resistance at the electrode/electrolyte interface according to the intercept of the spectrum on the real axis.¹³

The Nyquist plot of the AC/G supercapacitor shows not a very straight line in the low frequency region. An ideal capacitive behaviour of supercapacitor achieved when more vertical lines parallel to the imaginary axis in the low frequency region.³ In the high frequency region, the 1M LiPF₆ electrolyte resistance (representing the ohmic resistance of the electrolyte, separator) for AC/G electrode was 4.3 Ω. In addition, ~6.0 Ω of charge transfer resistance value, data taken at knee frequency of the Nyquist plot.

Overall, the major problem of an increased internal resistance for AC/G electrode might be due to the usage of binder material. In general, binder material brings impurities into the electrode and thus degrades electrochemical performance.¹⁴ Current supercapacitor is unlikely to perform as other individual carbon based supercapacitors. However, results in this work may bring a new perspective and idea of hybridising two different carbon materials.



4 Nyquist plot of AC/G electrode in LiPF₆ electrolyte

Conclusions

An EDLC type supercapacitor from activated carbon and graphene (AC/G) electrode was fabricated using conventional slurry technique. The fabricated supercapacitor has been examined for its electrochemical properties by means of CV, charge discharge and impedance analysis. The CV analysis showed the typical rectangular shaped curves suggesting the double layer capacitance behaviour of the electrode. AC/G electrode has a maximum gravimetric capacitance of 19.45 F g⁻¹ as examined by the CV measurement at a scan rate of 1 mV s⁻¹. The charge discharge analysis of AC/G electrode was performed and compared with different applied currents. The result obtained shows the discharge capacitance decreases with increases of current, and a large infrared drop, which possibly due to the internal resistance of the supercapacitor. In addition, from high frequency region in impedance analysis, electrolyte resistance for the supercapacitor was found to be 4.3 Ω, and ~6.0 Ω of charge transfer resistance value, a data taken at knee frequency of the Nyquist plot.

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