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Carbon nanomaterials derived from Malaysia's highway road asphalt waste as electrode for supercapacitor

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Abstract

Developing cost-effective and environmental friendly electrode material for supercapacitor is critical for energy storage technologies. The fabrication of asphalt waste carbon (AWC) combined with multi-walled carbon nanotube (MWCNT) supercapacitor electrode was performed by using conventional slurry technique. The AWC/MWCNT composite electrode was compared to that of non-mixed AWC electrode. For non-mixed AWC electrode, the specific gravimetric capacitance (C_{sp}) was 1.93 F g^{-1} at 1 mV s^{-1} scan rate and the C_{sp} obtained for AWC/MWCNT electrode was 62.94 F g^{-1}. From charge-discharge analysis, the AWC/MWCNT electrode showed nearly symmetrical triangular shapes at different current densities (0.5 to 15 A g^{-1}). It was also clear that the C_{sp} remains about 80% of the initial capacitance after 800 cycles at 15 A g^{-1} current density, indicating that AWC/MWCNT electrode possessed good ion accessibility and cycling stability.

1. Introduction

Carbon-based electrical energy storage devices have attracted increasing research interest owing to their unique characteristics such as long cycling stability, high specific capacitance, excellent mechanical and physical properties [1-3]. Among various energy storage devices, supercapacitor show unique characteristic including high power density and fast charging/discharging to be applied in hybrid electric vehicles and portable electronics compared with lithium ion batteries [4-6]. Generally, supercapacitor is classified into three types; electrochemical double-layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors [7]. The capacitance of EDLCs is based on accumulation of charges at the electrode-electrolyte interfaces meanwhile pseudocapacitors are based on the fast surface redox reactions [8].

Asphalt is a substance which classified as pitch has been used in road construction to create asphalt concreate by glue or binder mixed with aggregate particles. It is made from stones, sand and stone dust, mix all together by hot liquid asphalt cement and can be found in natural deposits or refine item. Asphalt typically contain about 80% by weight of carbon, 10% by of hydrogen, 6% of sulphur and the rest is small amount of oxygen and nitrogen and also trace amount of metals such as nickel, iron and vanadium [9]. In specific time, the asphalt concreates need to be removed from the road pavement (specific layer) due to poor quality. In order to avoid wastage, the asphalt waste can be reused for other application, in this case as electrode material for supercapacitor application. Furthermore, asphalt waste is 100% recycle materials and naturally goes under heat treatment which has been used over decade as construction material and road coating, and so, it is easy to get the material.

Here, we fabricate and characterize asphalt waste carbon (AWC) supercapacitor integrated with multi-walled carbon nanotube (MWCNT) as hybrid electrode by chemical activation and conventional coating technique. At 1 mV s^{-1}, the as-prepared hybrid electrode exhibits specific gravimetric capacitances of 62.94 F g^{-1}. Moreover, good capacitance performance and cycling stability of hybrid electrode suggest the high electron and ion conductivities of this unique and multifunctional AWC/MWCNT electrode. This study may open the new idea for the production of high performance carbon-based energy storage devices.

2. Experimental details

2.1. *Preparation of asphalt waste carbon (AWC) and AWC/MWCNT electrodes*

For preparing the asphalt waste carbon (AWC), the basic process was chemical activation. Asphalt waste was collected at nearby R&R Ayer Keroh along highway from Melaka to Seremban on 25 September 2015. These asphalt waste were removed from the road construction at thickness approximately of 180 mm. Then it was crushed with hammer followed by blended to turn asphalt waste into powder form. After that, the blended asphalt waste was washed with deionized water to remove dirt and dust from asphalt waste and was dried in drying oven at 100 °C for 12 hours to remove the moisture [10]. The cleaned blended asphalt waste was impregnated with 6M KOH then carbonized by using chemical activation at 650 °C with heating rate of 10 °C/min for 2 hours under constant flow of nitrogen atmosphere [11]. The AWC derived from asphalt waste by chemical activation method was washed by using deionized water until reached near to neutral. Then, the sample was dried in drying oven at 100 °C for 12 hours to remove the moisture [12]. The confirmation of ACW was confirmed by using Raman spectroscopy analysis.

2.2 *Electrochemical measurements of coin cell supercapacitors*

The working electrodes, AWC/MWCNT (denoted as sample 2) were prepared as follows; the as-prepared AWC powder, commercially available MWCNT powder (Sigma Aldrich), and polytetrafluoroethylene (85:10:5) were mixed in N-methyl pyrrolidone solvent. The resulting mixture was coated onto stainless steel mesh, which was followed by pressing to 3000 Psi using hydraulic hand press and dried at 120 °C for 6 h in oven (vacuum). The electrodes were measured in two-electrode system using an electrochemical workstation (Wonatech; 3000). The e1ectrolyte used for all cells was organic $LiPF_6$ (1M). The cell construction and the electrode fabrication were conducted in glove box with moisture content and air value below 10 ppm. The AWC electrode (denoted as sample 1) was also prepared for comparison of performance with the weight ratio of 95:5. The electrochemical measurements were carried out by cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD). The CV was recorded in potential window of 0 to 2.5 V at scan rates ranging from 1 to 100 mV s^{-1}. The GCD was tested at various current densities (1, 3, 5, 10 and 15 A g^{-1}). The gravimetric specific capacitance (C_{sp}) of the electrode is calculated based on CV curves from the Equation (1) [13];

$$Csp = \int_{E1}^{E2} i(E)dE \div 2(E2 - E1)mv \quad (1)$$

where (E1 and E2), i(E), ∫E1,E2 i(E)dE, (E2 - E1), m, and v are the cut off potential in CV, applied current, total voltammetric charges, potential window, mass of active material, and scan rate, respectively. Meanwhile, the C_{sp} of CD was determined by using Equation (2) [14];

$$Csp = \frac{2I}{m(dV/dt)} \quad (2)$$

where C_{sp}, I, m, dV, and dt, are the specific capacitance, applied current, mass of the active material (gram), potential window (volt), and discharge time (sec), respectively.

3. Results and Discussion

3.1. *Structural characterization*

In this work, the starting material was asphalt waste carbon (AWC), which was prepared by chemical activation. Based on the observation from naked eyes, the physical appearance of the obtained product is dull gray to black powder. Also, the product obtained was sieved by using 16 µm sizes. Fig. 1 shows the Raman spectra of as-prepared AWC which dominated by two intense peak located at about 1353 cm^{-1} (D-band) and 1588 cm^{-1} (G-band). These features indicate that sp^2-based carbon with a graphitic structure and possessing a medium value density of structural imperfection [15, 16]. The latter point was quantitatively evaluated by determining the integrated intensity ratio of D and G-bands (IG/ID). The IG/ID value of AC derived from asphalt waste is 1.11 which indicating the sample possess good quality structure of carbon materials [17].

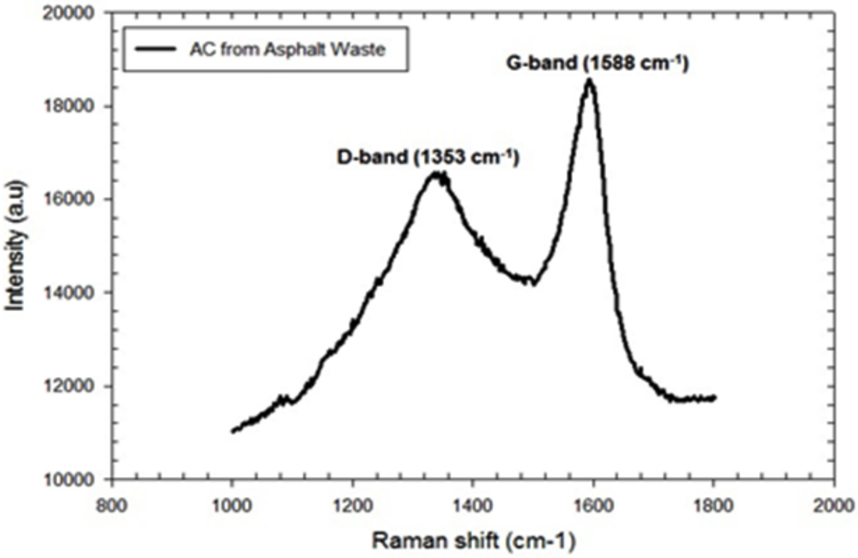

Figure 1: Raman spectrum of AWC powder

3.2 *Electrochemical performance*

We fabricated a high-voltage of pure AWC (sample 1) and AWC/MWCNT (sample 2) hybrid electrode by using two-electrode system for supercapacitor. Fig. 2a and Fig. 2b showed the CV profiles of pure AWC and AWC/MWCNT composite supercapacitor at the scan rate of 1 to 100 mV s^{-1}. Clearly, the symmetric device presented rectangular-like CV curves even at a high potential window up to 2.5 V indicating a nearly ideal supercapacitive characteristic. There has been a little distortion for sample 1 at the scan rate 50 and 100 mV s^{-1} due to decrease of electron transfer and electrolyte transportation [18]. Meanwhile, the CV curves show nearly rectangular shape and exhibits good electromechanical capacitive behavior in a wide range of scan rates [16]. The C_{sp} of sample 1 and sample 2 are 1.93, and 62.94 F g^{-1}, respectively. It showed that sample 2 has the highest C_{sp} and good rate stability compare to sample 1. This significant result showed that addition of MWCNT as conducting agent gives better stability in charge storage performance. It showed that the addition of MWCNT as conducting agent electrode gives rise to an increase in the C_{sp} on sample 2. Therefore, extra charge was stored on the electrode with the presence of MWCNT [19, 20]. Also, this enhanced electrochemical charge storage behavior might be due to the synergistic effect of AWC and MWCNT.

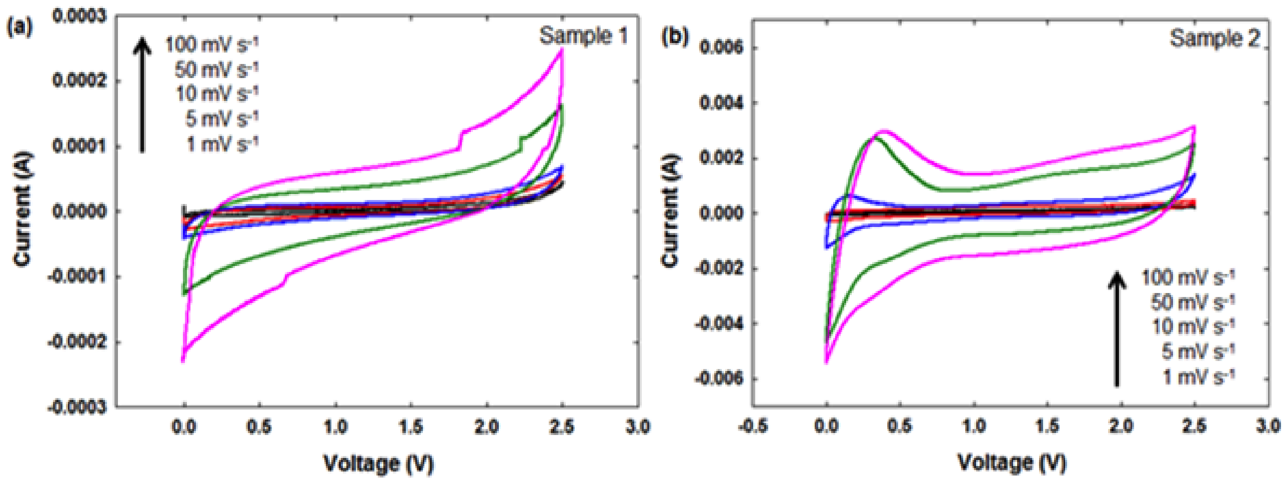

Figure 2: CV curves of (a) pure asphalt or AWC and (b) AWC/MWCNT hybrid electrodes at different scan rates

The capacitive performances of these AWC/MWCNT hybrid electrodes were further studied by galvanostatic charge–discharge (CD) measurements (Fig. 3). The symmetrical triangle feature and small IR drop at 0.5 A g^{-1} current density reconfirms its low internal resistance and typical capacitor behavior with C_{sp} value of 1.00 F g^{-1} (Fig. 3a). The small IR drop on sample 1 is probably due to the more disordered structured characteristics and lack of mesoporous for ion diffusion [18]. Moreover, CD measurements were also performed using different current densities in a potential window of 0 to 2.5 V as shown in Figure 3b for sample 2. The nearly symmetric CD profiles with a displayed the discharge curve of the sample 2 at various applied current densities (1 to 15 A g^{-1}). The C_{sp} of the sample 2 was 50.08, 28.75, 25.71, and 25.06 F g^{-1} at 1, 3, 5, and 10 A g^{-1}, respectively and retained 10.73 at 15 A g^{-1} indicating good rate capability. The nearly symmetric triangular shape indicates that sample 2 showed good electrical contact between electrode/electrolyte interfaces in $LiPF_6$ electrolyte [21]. This value is significantly better than sample 1. Notably, all the measurements indicate that this AWC/MWCNT hybrid electrode for both sample are ideal as electrode for supercapacitor.

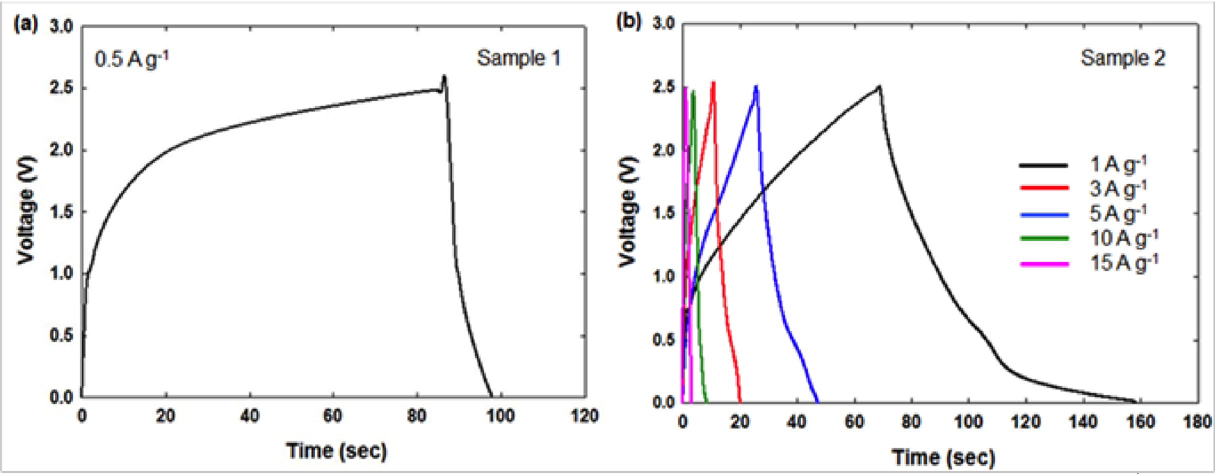

Figure 3: Galvanostatic charge–discharge curves of (a) pure asphalt or AWC electrode at 0.5 A g^{-1} and (b) AWC/MWCNT hybrid electrode in 1 M $LiPF_6$ at current density from 1 to 15 A g^{-1}

In view of the fact that cycling stability has always been regarded as a crucial role in supercapacitor applications, the long-term cycling test was carried out for 800 cycles. Notably, our supercapacitor is capable of retaining 80% of the initial discharge capacitance after 800 cycles at 15 A g^{-1}, showing an impressive lifespan and excellent cycling stability in 1 M $LiPF_6$ electrolyte (Fig. 4). These AWC/MWCNT hybrid electrodes showed high performance supercapacitor may be attributed from the ion diffusion along both the hybrid electrode [22]. The key parameter for high performance electrode is the modification of electrode structure for fast ion-transfer between the electrode-electrolyte interfaces [23].

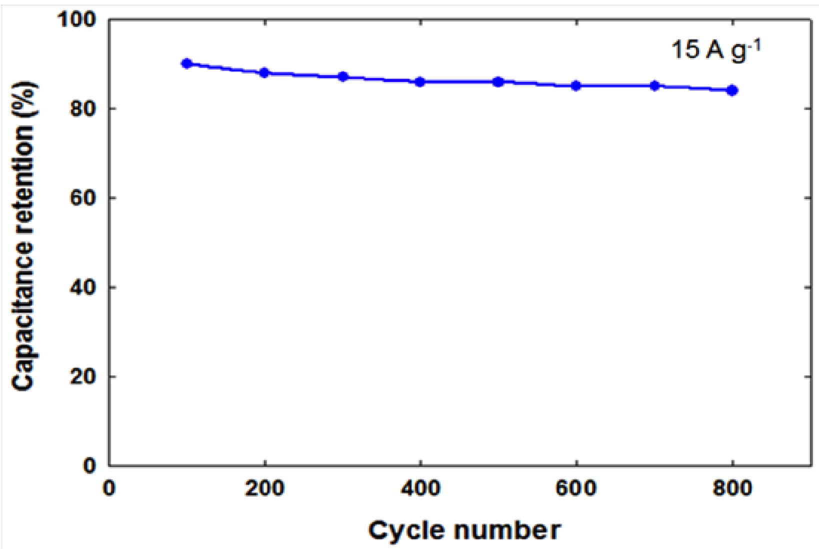

Figure 4: Cyclic stability of AWC/MWCNT hybrid electrode.

Conclusions

Asphalt waste carbon electrodes were synthesized from Malaysia's highway road asphalt waste as electrode for supercapacitor. The synthesis method involved chemical activation and slurry coating. The obtained activated carbon waste was measured by using organic electrolyte in two-electrode system. This is the first study on the preparation of carbon derive from asphalt waste in organic electrolyte for energy storage device. The specific capacitance of AWC/MWCNT hybrid electrode with 85:10:5 ratio of slurry composition was 62.94 F g^{-1} and good cycling stability. This study introduces a new idea of environmentally friendly by using waste material, cost-effective and the remarkable electrochemical performances of AWC/MWCNT hybrid supercapacitor will enable them a good practical application prospect.

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References

1. R.N.A.R. Seman, M.A. Azam, A.A. Mohamad, *Renew. Sustainable Energy Rev.* 75 (2016) 644.
2. J.H. Chang, Y.H. Hung, X.F. Luo, C.H. Huang, S. Jung, J.K. Chang, J. Kong, C.Y. Su, *RSC Adv.* 6 (2016) 8384.
3. H. Chen, T.N. Cong, W. Yang, C. Tan, Y. Li, Y. Ding, *Progress in Natural Science* 19 (2009) 291.
4. R.N.A.R. Seman, M.A. Azam, M.A. Mohamed, *Adv. Nat. Sci.: Nanosci. Nanotechnol* 7 (2016) 045016.
5. A.L. Ivanovskii, *Russ. Chem. Rev.* 81 (2012) 571.
6. J. Chen, C. Li, G. Shi, *J. Phys. Chem. Lett.* 4 (2013) 1244.
7. R.N.A.R. Seman, R.F. Munawar, J.A. Razak, N.N. Zulkapli, M.S.A. Bistamam, E. Talib, T.I.T. Kudin, N.S.A. Manaf, M.A. Azam, *Applied Mechanics and Materials* 761 (2015) 452.
8. M.A. Azam, N.H. Jantan, N. Dorah, R.N.A.R. Seman, N.S.A. Manaf, T.I.T. Kudin, M.Z.A. Yahya, *Mater. Res. Bull.* 69 (2015) 20.
9. J. Harvey and BW Tsai, *Transportation Research Record: J.Transportation Research Board* 1543 (1996) 38-45.
10. Y. Gao, L. Li, Y. Yin, Y. Wang, C. Yuan, Y. Wei, G. Chen, J. Ge, H. Lu, *Applied Energy* 153 (2015) 41.
11. I.I. Misnon, N.K.M. Zain, R.A. Aziz, B. Vidyadharan, R. Jose, *Electrochim. Acta* 174 (2015) 78.
12. Z. Li, J. Liu, K. Jiang, T. Thundat, *Nano Energy* 25 (2016) 161.
13. M.A. Azam, K. Isomura, A. Fujiwara, T. Shimoda, *J. New Mat. Electrochem. Syst.* 14 (2011) 173.
14. M.A. Azam, N. Dorah, R.N.A.R. Seman, N.S.A. Manaf, T.I.T. Kudin, *Mater. Technol.: Advanced Functional Materials* 30 (2015) A1.
15. H.B. Wu, H. Pang, X. Wen, D. Lou, *Energy Environ. Sci.* 6 (2013) 3619.
16. D. Wang, G. Fang, T. Xue, J. Ma, G. Geng, *J. Power Sources* 307 (2016) 401.
17. G. Tzvetkov, S. Mihaylova, K. Stoitchkova, P. Tzvetkov, T. Spassov, *Powder Technology* 299 (2016) 41.
18. A. Jain, C. Xu, S. Jayaraman, R. Balasubramanian, J.Y. Lee, M.P. Srinivasan, *Microporous and Mesoporous Materials* 218 (2015) 55.
19. H. Pan, J. Li, Y.P. Feng, *Nanoscale Res. Lett.* 5 (2010) 654.
20. Y. Liu, Y. Wang, G. Zhang, W. Liu, D. Wang, Y. Dong, *Mater. Lett.* 176 (2016) 60.
21. Y. Wang, H. Xuan, G. Lin, F. Wang, Z. Chen, X. Dong, *J. Power Sources* 319 (2016) 262.
22. P. Li, J. Liu, Y. Liu, Y. Wang, Z. Li, W. Wu, Y. Wang, L. Yin, H. Xie, M. Wu, X. He, J. Qiu, *Electrochim. Acta* 180 (2015) 164.
23. H. Feng, H. Hu, H. Dong, Y. Xiao, Y. Cai, B. Lei, Zheng M., *J. Power Sources* 302 (2016) 164.

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