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HIGH PERFORMANCE OF A FLEXIBLE GRAPHENE NANOPLATELETS SUPERCAPACITOR IN A STACKED CONFIGURATION

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HIGH PERFORMANCE OF A FLEXIBLE GRAPHENE NANOPLATELETS SUPERCAPACITOR IN A STACKED CONFIGURATION

By

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HIGH PERFORMANCE OF A FLEXIBLE GRAPHENE NANOPLATELETS SUPERCAPACITOR IN A STACKED CONFIGURATION

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July 2018

Chair: Assoc. Prof. Janet Lim Hong Ngee, PhD
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The energy density and working potential of conventional supercapacitor devices are in the range of 6–10 Wh/kg, which has hindered it to be implemented in electronic applications that required devices to run in a long durations at a higher voltage. Herein, we report a method for enhancing the energy density of a device through the parallel stacking of five copper foils electrodes coated with graphene nanoplatelets as electro-active material. Microporous papers immersed in 2 M of aqueous sodium sulphate electrolyte were then used as separators in between stacked copper foils to complete the supercapacitor device. The as-assembled supercapacitor had achieved a specific capacitance value of 142 F/g with low contact resistance of 0.05 Ω at 1 A/g. The supercapacitor yielded optimum specific energy and specific power density of 24.64 Wh/kg and 402 W/kg at 0.8 V, respectively. Furthermore, the utilization of copper foil current collector and microporous paper type separator give additional merit of flexibility to the supercapacitor when an unnoticeable difference in cyclic voltammetry curves was observed even at 45°, 90° and 180° bending angles. The supercapacitor bent up to 180° was able to maintain high capacitance retention up to 83% after 800 cycles of continuous charge discharge cycles. Interestingly, the working potential has been successfully increased up to 2.4 V when three of the stacked supercapacitors were connected in series by forming a tandem device while bended at 180 °C. Its potential for real application was manifested by the ability to light up a light-emitting diode for 40 s when charged for 60 s. Besides that, when comparing it with the commercial available supercapacitors (KEMET, ILLINOIS), the as-assembled supercapacitor was found to outperform it in terms of energy density. Overall, the electrochemical performance tests have demonstrated the high performance of aqueous-based flexible graphene nanoplatelets supercapacitor from stacked copper foils configuration. This was found to be mainly contributed to the proper selection of each supercapacitor components from the electrode active material, current collector, electrolyte and separator through systematic analysis of spectroscopy, microscopy and electrochemical characterizations. The study that has been discussed in this thesis could pave a way to be applicable in wearable electronic devices that required high energy density and working potential before it can be implemented.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master of Sains

FLEKSIBEL SUPERKAPASITOR PRESTASI TINGGI BERASASKAN NANOPLATELET GRAFIN DALAM KONFIGURASI TIMBUNAN SECARA SELARI

Oleh

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Julai 2018

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Ketumpatan tenaga dan potensi kerja peranti superkapasitor konvensional berada dalam lingkungan 6-10 Wh/kg, telah menghalangnya untuk dilaksanakan dalam aplikasi elektronik yang memerlukan peranti berjalan dalam tempoh yang panjang dan voltan yang lebih tinggi. Di sini, kami melaporkan satu kaedah untuk meningkatkan ketumpatan tenaga peranti melalui susunan selari lima elektrod kerajang tembaga yang dilapisi dengan grafin nanoplatelet sebagai bahan aktif elektro. Kertas mikroporos yang direndam dalam 2 M elektrolit natrium sulfat berair kemudian digunakan sebagai pemisah di antara kerajang tembaga yang disusun untuk melengkapkan peranti superckapasitor. Superkapasitor fabrikasi telah mencapai nilai kapasitif spesifik 142 F/g dengan rintangan sentuhan rendah 0.05 Ω pada 1 A/g. Superkapasitor menghasilkan tenaga tertentu yang optimum dan ketumpatan kuasa khusus 24.64 Wh/ kg dan 402 W/kg masing-masing pada 0.8 V. Selain itu, penggunaan pemungut arus tembaga dan pemisah mikroporos memberikan merit fleksibiliti tambahan kepada superkapasitor dengan menunjukkan perbezaan yang boleh dinafikan walaupun pada sudut lenturan 45°, 90° dan 180°. Superkapasitor dilentur pada sudut 180 ° mampu mengekalkan pengekalan kapasitif yang tinggi sehingga 83% selepas 800 kitaran caj berterusan. Menariknya, potensi kerja telah berjaya ditingkatkan sehingga 2.4 V apabila tiga superkapasitor yang disusun dihubungkan dengan siri dengan membentuk satu peranti tandem sementara bended pada 180°. Potensi untuk aplikasi nyata ditunjukkan dengan keupayaan untuk menyalakan dioda pemancar cahaya selama 40 saat apabila dikenakan 60 saat. Di samping itu, apabila membandingkannya dengan superkapasitor yang tersedia komersial (KEMET, ILLINOIS), superkapasitor yang direka menunjukkan prestasi yang ditandingi dari segi tenaga kuasa. Secara keseluruhannya, ujian prestasi elektrokimia telah menunjukkan prestasi tinggi fleksibel elektrokimia superkapasitor berasaskan akues nanoplatelet grafin daripada konfigurasi timbunan kerajang tembaga secara selari. Ini disumbang oleh pemilihan setiap komponen supercapacitor yang tepat, dari bahan aktif elektrod, pemungut, elektrolit dan pemisah semasa melalui analisis sistematik spektroskopi, mikroskopi dan pengkomersialan elektrokimia. Kajian yang telah dibincangkan dalam tesis ini boleh membuka jalan untuk digunakan dalam peranti elektronik yang boleh dipakai yang memerlukan ketumpatan tenaga yang tinggi dan potensi kerja pada masa depan.

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I certify that a Thesis Examination Committee has met on 4 July 2018 to conduct the final examination of Chiam Sin Ling on her thesis entitled "High Performance of a Flexible Graphene Nanoplatelets Supercapacitor in a Stacked Configuration" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science.

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LIST OF ABBREVIATIONS

BET	Brunauer-Emmett-Teller
LED	Light-emitting diode
CV	Cyclic voltammetry
EDL	Electrochemical double layer
EDLC	Electrochemical Double Layer Capacitor
EIS	Electrochemical impedance spectroscopy
E_D	Energy density
EDX	Energy-dispersive X-ray
FESEM	Field Emission Scanning Electron Microscopy (FESEM)
GCD	Galvanostatic charge discharge
GNPs	Graphene nanoplatelets
PVDF	Polyvinylidene fluoride
P_D	Power density
PC	Pseudocapacitor
Csp	Specific capacitance

CHAPTER 1

INTRODUCTION

In the past two decades, the rapid growth in the study of supercapacitors have been witnessed (Cao *et al.*, 2015; Chee *et al.*, 2015; Foo *et al.*, 2016; Kim & Kim, 2015; Liao *et al.*, 2015; Meher & Rao, 2011; Wang, 2004; Xia *et al.*, 2011). This are mainly contributed by their two attractive characteristics: fast charge/discharge rate (within few seconds to milliseconds) and long life cycles (usually more than 1,000,000 cycles) (Betrián, 2015; C. Liu *et al.*, 2010). Hence, this device can complementary to batteries when high power delivery, intermittent energy with variable power demands or long cycling stability are required, such as in the case of electric vehicles during accelerating or braking. Besides, supercapacitors were also being employed in the application with fluctuating load such as laptops, computers, portable media players and GPS as a power supply stabilizer. In the year 2013, Blueshift Company has offered to the market a portable speaker powered by supercapacitors (She, 2017). Yet, despite their promising features, the prevalent use of supercapacitors still being restricted. Two main challenges need to be overcome which is; i) energy density and ii) flexibility. The first challenge is in the fabrication of a single device that is able to store as much as energy as a battery yet remain the high power ability of supercapacitors (Peng *et al.*, 2015). The second requirement is in the fabrication of flexible supercapacitors to match the size limitation and flexibility requirement of modern electronic devices in various sector such as in automotive, healthcare, mobile device and biometrics (El-Kady & Kaner, 2013; Miller, 2012; Wang & Xia, 2013).

To address the first issue, electrode materials with a highly accessible surface area and excellent conductive are mandatory. As a unique 2D nanomaterials graphene nanoplatelets (GNPs), which comprised of few-nanometres thick graphene sheets are matching candidates attributed to their unique characteristics which include good electronic properties, high specific surface area and superior mechanical properties (Nieto *et al.*, 2012; Zhang *et al.*, 2014). Furthermore, the inherently rapid energy storage mechanism of GNPs where it only involves the simple movement of ions back and forth of the electrode surface, contributing to a system with high power density. Those unique structural characteristics and remarkable properties of GNPs will contribute to a stable charge storage system with fast ionic transport. Nonetheless, an individual supercapacitor is not able to single-handedly gives a comparable high energy storage than those provided by batteries. Thus, through stacking up the individual supercapacitor in parallel or/and connecting in series, the multiple of energy density or/and working potential can be achieved and tuned depend on the target application. This approach has made it more feasible in practical application (Peng *et al.*, 2015; Reddy *et al.*, 2008; Zhou *et al.*, 2012).

As for the second challenge, the real bottleneck hindering flexible supercapacitor based electronic devices from the practical application is to find a reliable material that possesses excellent conductivity, superior mechanical flexibility, and high stability in electrochemical environments (Gwon *et al.*, 2011; Shao *et al.*, 2015). Graphene nanoplatelets (GNPs) with exceptionally high mechanical strength material is one of the perfect candidates in the fabrication of flexible electrodes materials as its unique structure will prevent the electrode framework from being ruptured even being bent or twisted (Chee *et al.*, 2016; He *et al.*, 2012; Liu *et al.*, 2016; Wang *et al.*, 2009; Q. Zhou *et al.*, 2015). Apart from that, substrate materials do play a significant role in the fabrication of flexible electronic devices as it delivers mechanical flexibility and strength to the electrode components. Thus far, various substrate materials have been utilized in supercapacitors application which include the commonly reported nickel foam, carbon cloth and graphite sheet. This is mainly because of their good conductivity, high flexibility and high porosity (Chee *et al.*, 2016; Xu *et al.,* 2013). However, to the best of authors' knowledge, copper foil which is the commonly utilized current collector in lithium-ion batteries has not been used as substrate materials in the fabrication of supercapacitor (Li *et al.*, 2009; Lin *et al.*, 2015). Hence, in this work, we suggest the use of copper foil as another alternative, owing to their excellent electrical conductivity (second only to that of silver), flexibility and low cost technology ready for electronic fabrication. Therefore, the copper foil will open an insight as a good candidate for the fabrication of flexible supercapacitors.

In this study, GNPs was synthesized via a facile thermal exfoliation of expandable graphite. Then, the stacked GNPs symmetrical supercapacitor was assembled by the direct coating of obtained GNPs powder on the copper foil substrate using a binder. The small inclusion of 5 wt% of binder helped in providing intimate adhesion of the GNPs active materials on the surface of copper foil while maintaining the electrochemical performance. Furthermore, the utilization of GNPs as an active material and copper foil as a current collector successfully produce a flexible supercapacitor device with the ability to bend at various angle such as; 45°, 90° and 180°. To date, only a few stacking studies on supercapacitors have been reported (Peng *et al.*, 2015; Reddy *et al.*, 2008; Zhou *et al.*, 2012). For instance, stackable supercapacitor fabricated using laser induction method has shown an increase in performance compared to the single devices (Peng *et al.*, 2015). However, this method required up-scaling on the existing machines with limited yield and problems when dealing with the excessive heat production from the laser. Whereas, direct coating method reported here have been widely used in industry which already being scaled-up and possesses high yield of production. Thus, taking the benefits of direct coating method where its capability of forming double-sided GNPs-copper sheets electrode, enabling the fabrication of stacked GNPs based supercapacitors

.

Therefore, the objectives of this study are:

(a) To fabricate stacked graphene-based supercapacitors using graphene nanoplatelets (GNPs) active materials coated on the copper foil current collector.

(b) To analyse the electrochemical performance of stacked GNPs supercapacitors in terms of cyclic voltammetry (CV), galvanostatic charge discharge (GCD), electrochemical impedance spectroscopy (EIS), capacitance retention and flexibility.

(c) To compare the performance of the stacked GNPs supercapacitor with commercialized capacitors and to show its capability to light up a 2.4V LED bulb.

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