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GRAPHENE-BASED SUPERCAPACITORS APPLICATION FOR ENERGY STORAGE

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Abstract: Recent advances in graphene-based supercapacitor technology for energy storage application were summarized. The comparison of different types of electrode materials in such supercapacitors was performed. The supercapacitors with graphene-based electrodes exhibit outstanding performance: high charge–discharge rate, high power density, high energy density and long cycle-life, what makes them suitable for various applications, e.g. in transport, electrical vehicles or portable and flexible electronic devices.

Keywords: graphene, supercapacitor, energy storage.

1. INTRODUCTION

Rapid increase of energy consumption is one of the most important challenges in the twenty-first century. Therefore, the development of innovative energy conversion and storage systems is a crucial issue. The use of renewable energy sources, which in many cases seem to be an attractive alternative to the conventional solutions utilizing fossil fuels, requires high power and high energy density storage systems such as batteries or supercapacitors (ultracapacitors). Supercapacitors exhibit high charge–discharge rate, high power density, long cycle-life and no short circuit problem that commonly occurs for the batteries and they can be used in many different applications [1]. Although supercapacitors can provide outstanding power, they are not able to store as large amount of charge as in the case of the batteries, what makes them especially suitable for all the applications where the "power kick" is required. One interesting example of supercapacitor application is the so-called kinetic energy recovery system (KERS), where an energy storage device should be capable to store large amounts of energy in a short time. In this approach an electrical generator converts kinetic energy to electrical energy and stores it in a supercapacitor to be reused later. Also in various low-power devices (e.g. photographic flashes, static memories, MP3 players etc.), in which high capacity is not as important as high cycle-life and quick recharging, supercapacitor technology can be employed. Moreover, supercapacitors are also supposed to be used in smartphones, tablets, laptops or even electric cars, which currently run on batteries. From the practical point of view the most exciting advantage of this solution is the expected high recharge rate, what means that plugging for a few minutes would be enough to fully charge the device.

Generally, the construction of supercapacitors is similar to the construction of electrolytic capacitors. They consist of two electrodes immersed in the electrolyte and the separator (Fig.1). To enable the electrical charge carriers (ions) storage, porous material, such as activated charcoal, is used as the electrode. The electrodes are separated by a thin insulating layer enabling ionic transport. Because carbon is not a good insulator, the maximum operating voltage is limited to less than 3 V. Another disadvantage of using this material as the electrode is the size of charge carriers, which disables their penetration into the smaller pores, resulting in a reduced storage capacity.

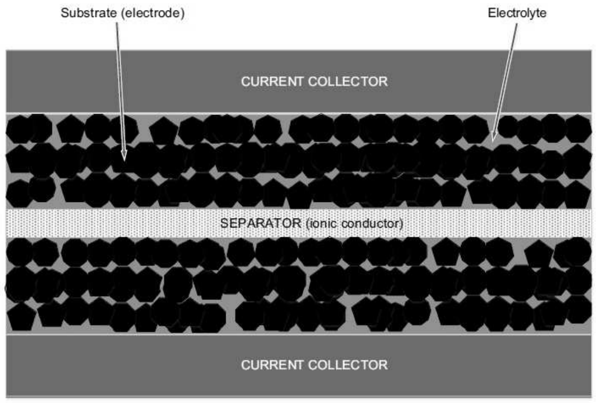

Fig.1. Schematic diagram of symmetric supercapacitor [1]

It is commonly believed that graphene is one of the most promising materials for the supercapacitor technology. The aim of this paper is to present recent advances in graphene-based supercapacitors application for energy storage.

2. ELECTRODE MATERIALS

Graphene is two-dimensional carbon monolayer structure exhibiting the most outstanding properties, that is, chemical stability, high electrical and thermal conductivity, extreme mechanical strength and large tunable surface area. These properties enable graphene and graphene-based materials to be applied for both the energy generation and storage. Graphene material is often suggested to replace the activated carbon in supercapacitors, mainly because of its higher relative surface area [2]. It is possible to produce low-cost graphene-based materials in a large scale after the improvements in the exfoliation and reduction process of graphite oxide (GO). Many different techniques have been proposed to produce graphene-based materials for supercapacitors electrodes. It is worth to mention some of them, namely, chemical reduction in hydrazine [3], microwave exfoliation of GO (MEGO) [4,5], liquid-electrolyte mediated chemically covered graphene preparation (EM-CCG) [6], laser scribing (LSG) [7] and one-step hydrogen annealing (HAG) [2]. Details of MEGO, LSG and HAG methods are shown in Figures 2-4.

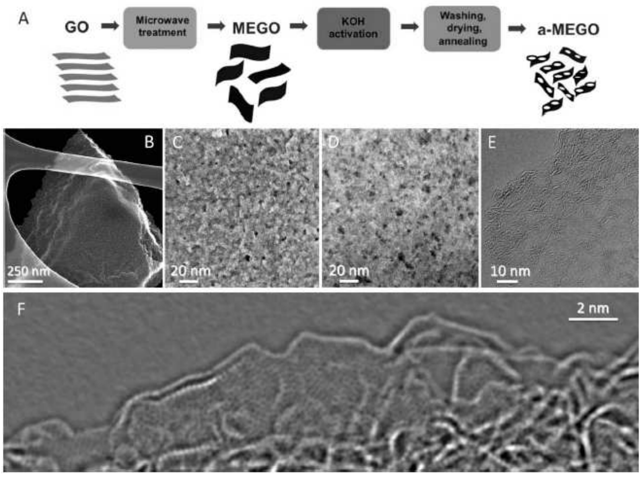

Fig. 2. Diagram of microwave exfoliation-reduction (MEG) process of graphite oxide (A) and images of different areas of the electrode from SEM (B-E) and STM (F) analysis [4]

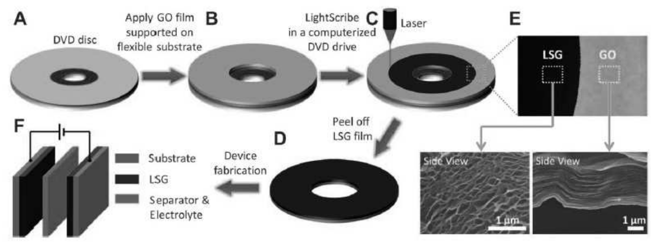

Fig. 3. Diagram of laser scribing of graphite oxide (LSG) process and SEM images of different areas of the material [7]

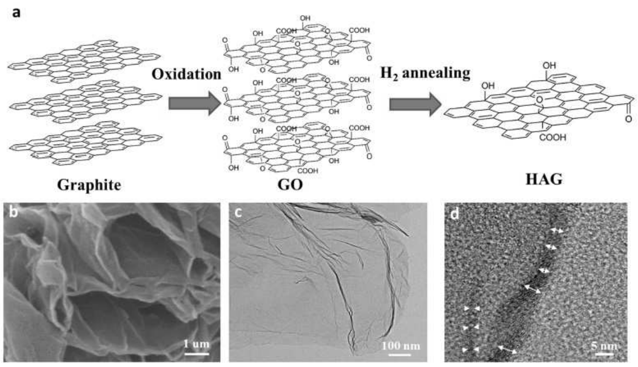

Fig. 4. Diagram of hydrogen annealing (HAG) of graphite oxide (a) and images of different areas of the electrode from SEM (b) and TEM (c) analysis [2]

3. PERFORMANCE

A comparison of various types of graphene-based supercapacitors is presented in Table 1. As can be noticed, the best supercapacitor performance was obtained for HAG electrodes and ionic liquid $EMIMBF_4$ (1-ethyl-3-methylimidazolium tetrafluoroborate) as an electrolyte. The porous graphene material was characterized to have an average pore size of a few nanometers with the uniform distribution of the size. This kind of electrode enables to achieve simultaneously a high energy density and power density. It was also shown that the use of the $EMIMBF_4$ electrolyte results in higher energy storage capability and wider temperature tolerance when compared with aqueous electrolytes. It was estimated that in HAG supercapacitors the energy density could be approximately one order of magnitude higher than in the commercial ones having the activated carbon as the electrode material [8]. This excellent performance is achieved as a result of maximum ion access due to the almost ideally matching size of pores [2].

Table 1. Comparison of graphene-based supercapacitors [2]

Material	Electrolyte	Specific capacitance ($F\ g^{-1}$)	Energy density ($W\ h\ kg^{-1}$)	Power density ($kW\ kg^{-1}$)
Graphene (curved) [3]	$EMIMBF_4$	154.1	85.6	1.14
MEGO [4]	Organic	166	~70	-
LSG [7]	Organic	276	28.33	-
EM-CCG [6]	Organic	167.1	88.24	6.88
HAG [2]	$EMIMBF_4$ $LiPF_6$	306.03 111.10	148.75 31.39	30.95 30.65

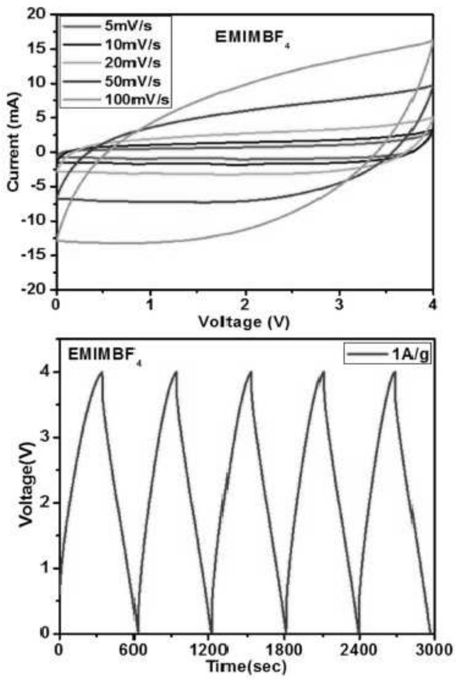

Fig. 5. Current *vs.* voltage characteristics and charge–discharge curve of HAG electrode [2]

The current-voltage characteristics and galvanostatic charge–discharge curve of HAG supercapacitor utilizing the $EMIMBF_4$ electrolyte are shown in Figure 5. It is apparent from the measurements that this type of device can work up to a relatively high voltage (~4.3 V) because of the moderate conductivity of the applied electrolyte. One can also see that the linear discharging curve is similar to the typical double-layer capacitor (EDL) characteristics. The visible drop of the voltage at the beginning of the discharging process is caused by the equivalent series resistance (ESR) [2].

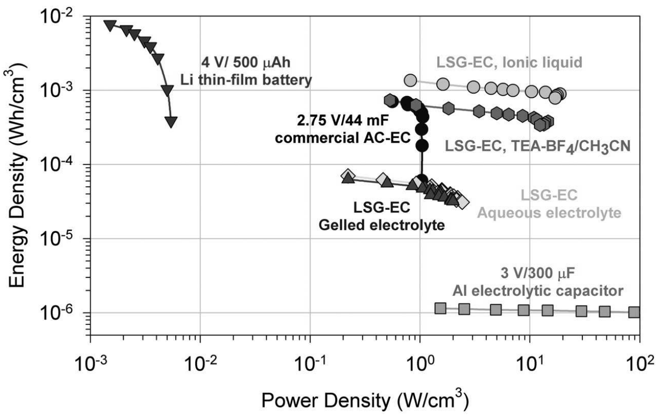

Fig.6. Comparison of energy and power densities of LSG supercapacitors with commercial activated-carbon electrochemical capacitors (AC-EC) and a lithium thin-film battery [7]

Although the LSG electrodes do not provide as good performance as the HAG ones, they can be potentially used as energy storage devices for various applications in microelectronics, where a high-power is required. As can be noticed from Figure 6, the energy densities in LSG supercapacitors can reach the values approximately two times higher than those of commercial activated-carbon electrochemical capacitors (AC-EC). Moreover, the power density of laser-scribed supercapacitors is about twenty times higher than in the case of the AC-EC devices and three orders of magnitude higher than in lithium batteries. When the gelled polymer electrolyte of polyvinyl alcohol (PVA)-H_3PO_4 is used, the weight and the thickness of the supercapacitor can be significantly reduced. It was also proven that such a device can work under mechanical stress with comparable efficiency [7].

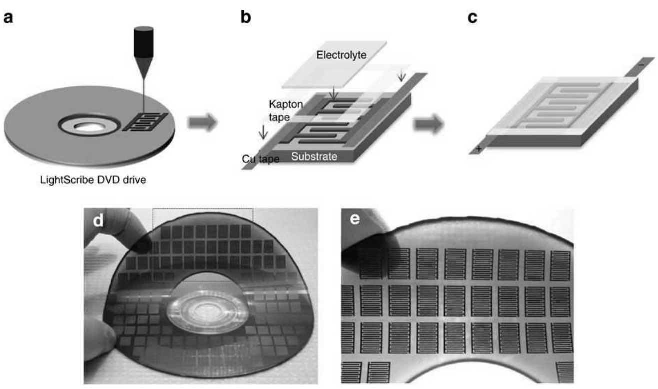

Fig.7. Schematic diagram of flexible LSG micro-supercapacitor production [9]

The LSG supercapacitors are supposed to be a very promising energy storage device for future flexible electronics and on-chip applications. It was demonstrated that a standard LightScribe DVD drive enables preparation of more than one hundred micro-supercapacitors by direct laser writing on GO films in a very short time (Fig. 7) [9].

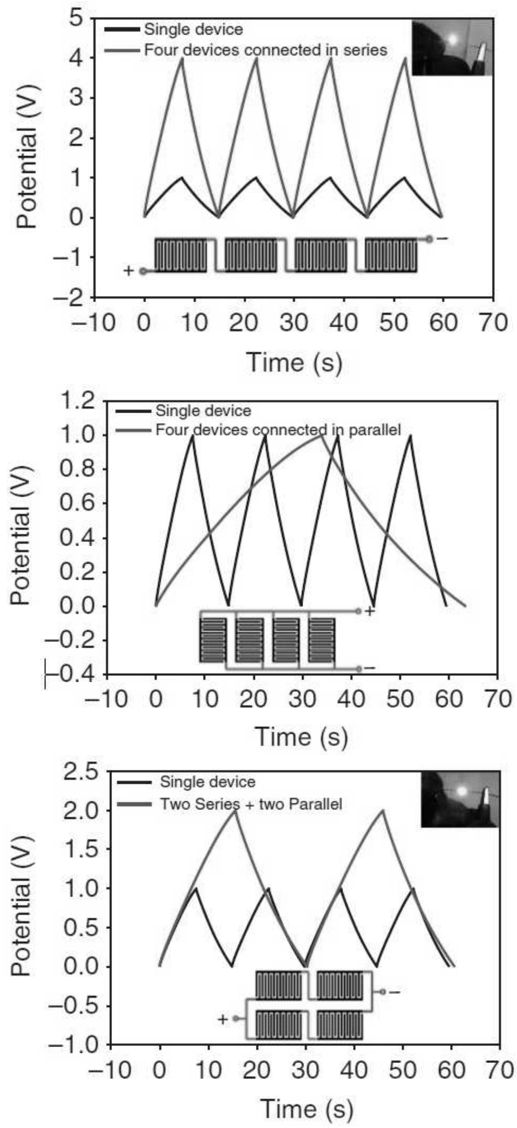

Fig.8. Charge-discharge curves for four LSG micro-supercapacitors connected in series, in parallel and in a combination of series and parallel [9]

The charge-discharge curves of either the single micro-supercapacitors or the ones connected in series, in parallel and in serial/parallel combination exhibit practically ideal triangular shape which indicates excellent properties of such devices (Fig.8). Noteworthy, no voltage balance was necessary to prevent the individual cell from going into over-voltage, what is very common in series connections [9].

4. CONCLUSIONS

In this short review recent advances in graphene-based supercapacitors were presented. Significant efforts have been made over the last few years to design and develop various types of supercapacitors for energy storage applications. It has been demonstrated that graphene-based materials are excellent candidates for electrode materials in such devices [10]. Further intensive research work is still necessary to improve the overall performance, develop a low-cost mass production process to enable the application of graphene-based supercapacitors e.g. in transport, electrical vehicles and even in portable or flexible electronic devices.

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ZASTOSOWANIE SUPERKONDENSATORÓW NA BAZIE GRAFENU DO MAGAZYNOWANIA ENERGII

W artykule podsumowano najnowsze osiągnięcia w dziedzinie technologii supekondensatorów na bazie grafenu. Porównano różne rodzaje materiałów wykorzystywanych jako elektrody w tego typu kondensatorach. Superkondensatory grafenowe charakteryzują się doskonałymi parametrami: dużą szybkością ładowania i rozładowania, dużą gęstością mocy, dużą gęstością energii oraz dużą żywotnością, co sprawia, że urządzenia takie mogą mieć zastosowanie na przykład w transporcie, pojazdach elektrycznych lub w przenośnych i giętkich urządzeniach elektronicznych.

Słowa kluczowe: grafen, superkondensator, magazynowanie energii.