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A Review of Graphene-Based Electrochemical Microsupercapacitors

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Abstract: The rapid development of miniaturized electronic devices has led to a growing need for rechargeable micropower sources with high performance. Among different sources, electrochemical microcapacitors or microsupercapacitors provide higher power density than their counterparts and are gaining increased interest from the research and engineering communities. To date, little work has appeared on the integration of microsupercapacitors

onto a chip or flexible substrates. This review provides an overview of research on microsupercapacitors, with particular emphasis on state-of-the-art graphene-based electrodes and solid-state devices on both flexible and rigid substrates. The advantages, disadvantages, and performance of graphene-based microsupercapacitors are summarized and new trends in materials, fabrication and packaging are identified.

Keywords: Microsupercapacitors · Supercapacitors · Energy storage · Graphene · Nanomaterials · Electrochemistry

1 Introduction of Supercapacitors

The need to store and use energy on diverse scales in a modern technological society necessitates the design of large and small energy systems, among which electrical energy storage systems such as batteries and supercapacitors have attracted much interest in the past several decades [1]. Supercapacitors, also known as ultracapacitors, or electrochemical capacitors, with fast power delivery and long cycle life, are playing an important role in complementing or even replacing batteries in many applications [1,2]. The first patent on supercapacitors was granted to Becker at General Electric Corp. in 1957 [3], in which he proposed a capacitor based on porous carbon material with high surface area. Later in 1969, first attempts to market such devices were undertaken by SOHIO [4]. Between the late 1970s and the 1980s, Conway successfully fabricated supercapacitors with high specific capacitance and low internal resistance using RuO₂ as an active material [5]. In the 1990s, supercapacitors began to attract attention because of the emergence of hybrid electric vehicles [6]. Supercapacitors offered the promise to supplement batteries and fuel cells in hybrid electric vehicles in providing the necessary power for acceleration, and additionally to allow for the recuperation of brake energy. These promising studies prompted the U.S. Department of Energy to initiate supercapacitor development programs. A comprehensive review of the historical background, properties, and principles of supercapacitors has been provided by Conway [1].

Supercapacitors effectively fill the gap between batteries and conventional capacitors (e.g., electrolytic capacitors or metalized film capacitors) [6]. They provide higher power density than batteries and fuel cells and higher energy density than conventional capacitors, while offering long lifetimes. In recent years, much progress has

been achieved in both theoretical understanding [7–12] and experimental design [2,13,14] of high-performance supercapacitors. Meanwhile, their low energy density and high production costs have emerged as major challenges for the future development [1,2,6,13].

As the size of portable electronic devices becomes smaller, low-power integrated circuits in devices such as sensors, microprocessors and wireless communication chips will make increasing use of miniature embedded microelectromechanical systems (MEMS) that operate in controlled/uncontrolled environments to gather, process, store and communicate information. Thus, there is a demand for integrated power sources to meet biological [15], medical [16] and environmental [17] applications. Micropower systems can be fabricated with length scales in the micrometer range and with improved performance by decreasing diffusion lengths to achieve this purpose. Among these micropower systems, microbatteries [18–20], microsupercapacitors [19,21], microfuel cells [22]

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Chuizhou Meng received the B. S. degree and Ph.D. degree in physics from Tsinghua University, Beijing, China, in 2006 and 2011, respectively. During his graduate research, he focused on the fabrication of advanced CNT/polymer nano-composites and their application in energy harvesting, conversion and storage. In August 2011, he became a post-doctoral research associate in the Center for Implantable Devices and Weldon School of Biomedical Engineering, Purdue University, West Lafayette, IN, USA. His current research interest focuses on the fabrication of micro-supercapacitors and their integration with antenna, MEMs, ASICs into miniature RF-wireless implantable medical devices for clinical applications such as targeted reinnervation, epilepsy, glaucoma, and cardiology.



Ron Reifenberger is a professor of Physics at Purdue University and a member of Purdue's Center for Sensing Science and Technology. He received his undergraduate degree in Physics from John Carroll University in 1970 and his PhD in Physics from the University of Chicago in 1976. He joined the Physics faculty at Purdue in 1978 following a two-year post-doctoral appointment in the Physics Department at the University of Toronto. Upon joining the faculty at Purdue, Reifenberger initiated a program to measure photo-induced field emitted electrons from a variety of metals. Since 1986, Reifenberger's scanning probe group has been active in furthering inter-disciplinary nanoscale research at Purdue by establishing collaborations with faculty throughout campus. His group has focused on research problems that emphasize the role of scanning probe microscopy (SPM) as one of the key enablers of nanotechnology. His current research is focused on non-linear dynamics of SPM cantilevers, micro patterning of substrates for the rapid detection of targeted bacteria, and fundamental measurements related to current flow in molecules, carbon nanotubes and Au nanocluster networks.



and piezoelectric energy harvesters [23] have been explored in the recent years. Microbatteries based on thin film solid-state Li/TiS were introduced to provide power for microsystems in the late 1990s [20], and since then the use of enhanced materials has further improved their performance [24,25]. Despite these improvements, inherent problems associated with microbatteries remain, making them unable to satisfy various requirements of autonomous microsystems (e.g., stability over long-term cycling, high power-high charge/discharge rates, and immunity to severe environments, particularly low tempera-

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Timothy S. Fisher (PhD in Mechanical Engineering, 1998, Cornell) joined Purdue's School of Mechanical Engineering and Birk Nanotechnology Center in 2002 after several years at Vanderbilt University. He is an Adjunct Professor in the International Centre for Materials Science at the Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR) and co-directs the JNCASR-Purdue Joint Networked Centre on Nanomaterials for Energy. From 2009 to 2012, he served as a Research Scientist at the Air Force Research Laboratory's newly formed Thermal Sciences and Materials Branch of the Materials and Manufacturing Directorate. In 2013 he became the James G. Dwyer Professor in Mechanical Engineering at Purdue. Prior to his graduate studies, he was employed from 1991 to 1993 as a design engineer in Motorola's Automotive and Industrial Electronics Group. His research has included studies of nanoscale heat transfer, carbon nanomaterial synthesis, coupled electro-thermal effects in semiconductor and electron emission devices, energy conversion and storage materials and devices, microfluidic devices, biosensing, and related computational methods ranging from atomistic to continuum scales.



tures). Microsupercapacitors, on the other hand, can couple with microbatteries and energy harvesting microsystems to provide high peak power, long cycle life, and high charge/discharge rates, while maintaining reasonable energy densities for practical applications in microsystems. Moreover, today's technological advancements in micro and nano-scale fabrication provide a solid foundation for fabrication of microsupercapacitors. Thus it is reasonable to project that microsupercapacitors will satisfy a variety of micropower demands and will complement or even replace microbatteries in electrochemical energy storage systems where high power delivery is required in short times.

Figure 1 contains a customary Ragone plot that compares the volumetric specific energy and power densities of a Li thin film battery, a commercial 3.5 V/25 mF supercapacitor, a 63 V/220 mF electrolytic capacitor, and a microsupercapacitor based on activated carbon (AC), a typical electrode material, cited from [26]. Electrolytic capacitors have higher charge/discharge rates and thus higher power densities than AC microsupercapacitors, but their specific energy is more than two orders of magnitude lower. Meanwhile, lithium batteries and conventional supercapacitors do not provide the ultrafast charge/discharge rates demonstrated by AC microsupercapacitors. Moreover, the specific energy of AC microsupercapacitors is roughly two orders of magnitude higher than commercial conventional supercapacitors and even higher than Li thin film batteries.

In this review, we highlight recent developments in on-chip microsupercapacitor research. A particular focus is on electrochemical performance of graphene-based electrode materials. Section 1 contains an introductory background on supercapacitors and particularly microsupercapacitors. Section 2 briefly discusses the fundamentals of supercapacitors, while Section 3 highlights structural dif-

ferences between conventional (or macro-) and microsupercapacitors. Section 4 reviews graphene-based electrode materials and their electrochemical performance. Section 5 reports developments in solid-state graphene-based microsupercapacitors on both flexible and rigid substrates while Section 6 summarizes fabrication techniques of graphene-based electrodes. Finally, Section 7 contains conclusions and a forward-looking outlook.

2 Fundamentals of Supercapacitors

2.1 Basic Structures and Performance Evaluation

A conventional supercapacitor consists of two electrodes (symmetric or asymmetric) and a separator sandwiched between them that are sealed in organic or aqueous electrolyte liquid. Recently, all-solid-state supercapacitors have also been designed using solid-state gel or polymer electrolytes. The configuration of a conventional supercapacitor is shown in Figure 2. Unlike electrolytic capacitors, where charge accumulates on two conductors separated by a dielectric, supercapacitors store charge at the interface between an electrode and an electrolyte solution. When charged, the negative ions in the electrolytes diffuse to the positive electrode, while the positive ions diffuse to the negative electrode to create two separate layers of capacitive storage. Consequently, in such a two-terminal configuration each electrode-electrolyte interface represents a capacitor so that the complete cell can be considered as two capacitors in series, as shown in Figure 2. The cell capacitance for the supercapacitor cell can be calculated from:

$$\frac{1}{C_{\text{cell}}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

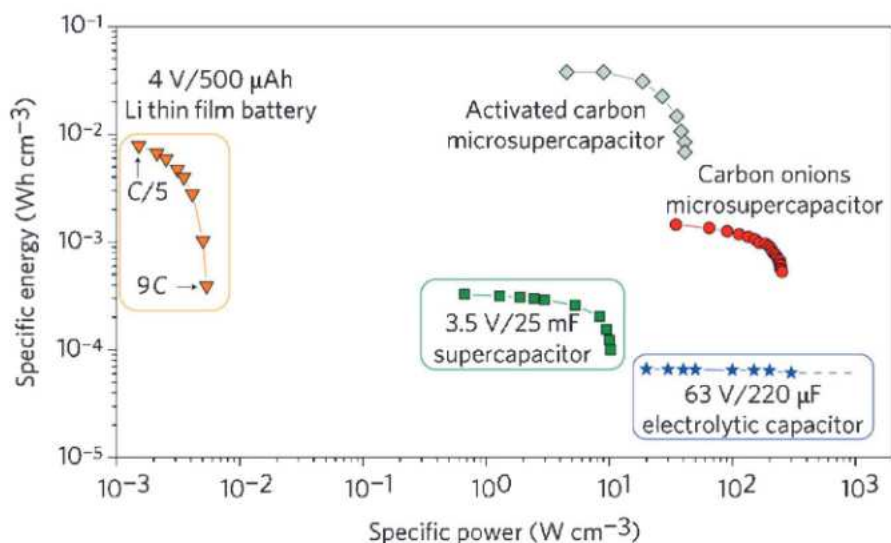


Fig. 1. Comparative Ragone plot of a Li thin film battery, commercial supercapacitor, electrolytic capacitor and AC microsupercapacitor, reprinted with permission from [26].

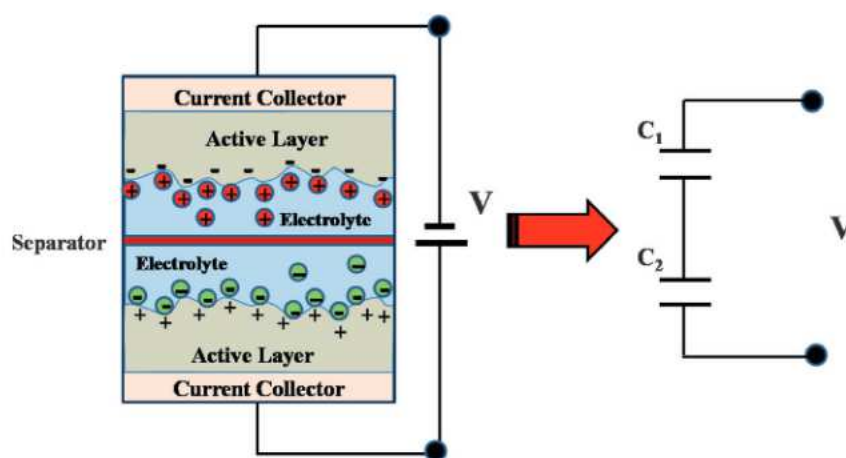


Fig. 2. Schematic representation of a supercapacitor cell.

where C_{cell} is the capacitance of the two-terminal device and C_1 and C_2 represent the capacitances of the two electrodes, respectively [13,14,27].

Supercapacitors can be classified into two main types in terms of working mechanism: (a) electric double-layer capacitors and (b) pseudocapacitors. Electric double-layer capacitors (EDLCs) store energy through ion adsorption; namely, the charge accumulations are achieved with electrostatically positive and negative charges separately residing on interfaces between electrolyte and electrodes. The charge transfer process in EDLCs is non-faradic, i.e., ideally no electron transfer takes place across the electrode interface. Pseudocapacitors store energy through fast redox reactions between the electrolyte and electroactive materials on the electrode surface. Electron transfer causes charge accumulation, and the charge transfer process is faradic in nature.

For electric double-layer supercapacitors, the specific capacitance C (in F/g) of each electrode is approximated by that of a parallel-plate capacitor [28,29]:

$$C \approx \epsilon_r \epsilon_0 A / dm \quad (2)$$

where ϵ_r is the relative permittivity, ϵ_0 is the permittivity of vacuum (8.85×10^{-12} F/m), A is the surface area of the electrode accessible to the electrolyte ions, m is the mass of active materials in grams; and d , the Debye length, is used to estimate the charge separation distance [2,29]. The Debye length is usually approximated as:

$$d \approx \frac{r}{2e^2 z^2 N_A c_1} \quad (3)$$

where ϵ_r is the relative dielectric constant, k_B is the Boltzmann constant (1.38×10^{-23} J/K), T is the temperature in Kelvin, e is the elementary electronic charge (1.60×10^{-19} C), z is the (integer) valence of the ionic species, N_A is the Avogadro constant (6.02×10^{23} mol $^{-1}$), and c_1 is the bulk molar concentration (in moles/m 3) of the ionic spe-

cies. Typically, $d = 0.3$ nm for a 1 M concentration of a monovalent ionic species in water ($\epsilon_r = 80$) at 25 °C. In electric double-layer capacitors, according to Equation 2, high specific surface area (typically > 1500 m 2 /g) of the active electrode materials and charge separations d close to atomic dimensions are the most important factors contributing to extremely high capacitance [14,30].

For pseudocapacitors, faradaic capacitance (C_F) is calculated from the charge stored (Dq) and the change in potential (DV) by [1,5]:

$$C_F \approx \frac{\partial Dq}{\partial DV} \quad (4)$$

Experimentally, specific capacitances can be calculated from both cyclic voltammetry (CV) and galvanostatic charge/discharge. Capacitances derived from CV tests are calculated from [31,32]:

$$C \approx \frac{1}{2s} \frac{\int_{V_h}^{V_l} I(V) dV}{V_h - V_l} \quad (5)$$

where s is the scan rate in V/s, V_h and V_l are high and low potential limits of the CV tests in V, I is the instantaneous current in CV curves, and V is the applied voltage in V. Capacitances derived from galvanostatic charge/discharge tests are calculated from [33]:

$$C \approx I_d / Mv \quad (6)$$

where I_d is the discharge current in A, and v is the slope of the discharge curve after the initial voltage drop (IR drop, V_{IR}) of the discharge curves. The internal resistance R (in Ω) is determined from the voltage drop at the beginning of a discharge curve by [34,35]:

$$R \approx DV_{IR} / 2I_d \quad (7)$$

where DV_{IR} is the voltage dropped across the internal resistance in V. The factor of "2" is associated with the in-

