Journal of Energy Chemistry xxx (2017) xxx–xxx

Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

http://www.journals.elsevier.com/journal-of-energy-chemistry/

Review

Graphene-based materials for flexible energy storage devices

Kena Chen[a], Qingrong Wang[a], Zhiqiang Niu[a,*], Jun Chen[a,b]

[a] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China
[b] Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Tianjin 300071, China

ARTICLE INFO

Article history:
Received 14 August 2017
Revised 25 August 2017
Accepted 31 August 2017
Available online xxx

Keywords:
Graphene
Flexible
Energy storage device

ABSTRACT

The booming developments in portable and wearable electronics promote the design of flexible energy storage systems. Flexible supercapacitors and batteries as promising energy storage devices have attracted tremendous attention. As the key component of both supercapacitors and batteries, electrode materials with excellent flexibility should be considered to match with highly flexible energy storage devices. Owing to large surface area, good thermal and chemical stability, high conductivity and mechanical flexibility, graphene-based materials have been widely employed to serve as promising electrodes of flexible energy storage devices. Considerable efforts have been devoted to the fabrication of flexible graphene-based electrodes through a variety of strategies. Moreover, different configurations of energy storage devices based on these active materials are designed. This review highlights flexible graphene-based two-dimensional film and one-dimensional fiber supercapacitors and various batteries including lithium-ion, lithium–sulfur and other batteries. The challenges and promising perspectives of the graphene-based materials for flexible energy storage devices are also discussed.

Kena Chen received her B.S. degree in chemistry from Qufu Normal University (2015). She then joined the Key Laboratory of Advanced Energy Materials Chemistry in Nankai University under the supervision of Prof. Zhiqiang Niu. Her research focuses on the design and preparation flexible lithium–sulfur batteries based on graphene.

Qingrong Wang received his B.S. degree in chemistry from Shandong University (2015). He then joined the Key Laboratory of Advanced Energy Materials Chemistry in Nankai University under the supervision of Prof. Zhiqiang Niu. His research focuses on the design and preparation flexible supercapacitors based on graphene.

Zhiqiang Niu is a Professor at the College of Chemistry, Nankai University. He received his Ph.D. degree from the Institute of Physics, Chinese Academy of Sciences in 2010 under the supervision of Prof. Sishen Xie. After his postdoctoral research in the School of Materials Science and Engineering, Nanyang Technological University (Singapore, co-supervisor: Prof. Xiaodong Chen), he started his independent research career as Hundred Young Academic Leaders of Nankai University in 2014. He has been awarded the National Youth Thousand Talents of China (2015). He has published more than 40 peer-reviewed journal papers and 3 book chapters on nanocarbon materials and energy storage devices. His research interests include nanocarbon materials and advanced energy storage devices.

Jun Chen is a Cheung Kong Scholar Professor and the Director of the Key Laboratory of Advanced Energy Materials Chemistry (KLAEMC) at Nankai University, a Principle Investigator at Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), and Chairman of the Chinese Society of Electrochemistry. He obtained his B.Sc. and M.Sc. degrees from Nankai University in 1989 and 1992, respectively, and his Ph.D. from Wollongong University (Australia) in 1999. He held the NEDO fellowship at National Institute of AIST Kansai Center (Japan) from 1999 to 2002. He has been working as a full professor on energy chemistry in Nankai University since 2002. His research activity focuses on nanostructured materials for electrochemical energy storage and conversion such as batteries, supercapacitors, fuel cells, and solar cells. He is a FRSC and a member of the Editorial Board of *Nano Research, Solid State Sciences* and *Journal of Energy Chemistry*.

* Corresponding author.
E-mail address: zqniu@nankai.edu.cn (Z. Niu).

https://doi.org/10.1016/j.jechem.2017.08.015

Please cite this article as: K. Chen et al., Graphene-based materials for flexible energy storage devices, Journal of Energy Chemistry (2017), https://doi.org/10.1016/j.jechem.2017.08.015

1. Introduction

The recent dramatic developments in portable and wearable electronics have motivated the urgent demand for flexible energy storage devices [1–6], which must be capable of maintaining their electrochemical stability under different deformations (bending, twisting, folding, stretching, etc.) [7–12]. Up to now, tremendous progress has been achieved in designing a variety of flexible energy storage systems, such as lithium-ion batteries (LIBs) and supercapacitors (SCs) [7,13–15]. LIBs have been regarded as one of the most promising candidates for energy storage devices due to their high energy density [16–18]. Since SCs possess high power density and stable cycling life compared with LIBs, they have also sparked considerable interest for scientific research [19–21]. Electrode materials, generally as the crucial components of flexible energy storage devices, should endow themselves with outstanding conductivity, good mechanical properties as well as high electrochemical stabilities. However, the fabrication of conventional SC and LIB electrodes was usually a slurry-casting process, which involves mixing the active materials with conductive additives and polymer binders and then casting the slurry on the metallic current collector. In this case, active materials are easily delaminated from current collectors, leading to the degradation of electrode performance. Moreover, it is difficult to recover to their original states when they suffer from repetitive deformations. Therefore, the rational design of mechanically flexible electrode materials together with desired structures plays a pivotal role in developing high-performance flexible energy storage devices.

Graphene, a two-dimensional (2D) monolayer of carbon atoms with packed honeycomb lattices, displays abundant fascinating properties, such as large surface area, good thermal and chemical stability, high conductivity, and mechanical flexibility [22,23]. Meanwhile, the unique features of graphene and its derivatives, such as graphene oxide (GO) and reduced graphene oxide (RGO) (Fig. 1), make it possible to serve as the building blocks to further construct macroscopic self-supporting graphene materials, which are promising candidates of the electrodes for flexible SCs and LIBs. Recently, although a great deal of efforts have been devoted to fabricating graphene-based electrode materials and designing flexible SCs and LIBs based on them [7,25,26], it is noted that the reviews about the design of flexible graphene-based materials into flexible energy storage devices with different configurations are still rare.

In this review, we will summarize the recent research achievements on the rational design of flexible graphene-based electrodes and the corresponding configurations of flexible energy storage devices, including SCs and batteries. In particular, flexible graphene-based 2D film and one-dimensional (1D) fiber SCs are highlighted. Similarly, flexible LIB and other battery devices beyond LIBs, such as lithium–sulfur (Li–S), lithium–O_2 (Li–O_2) and sodium-ion batteries (SIBs) on the basis of graphene-based films and fibers are also introduced and discussed. Finally, we discuss the challenges and promising perspectives of the graphene-based materials for flexible energy storage devices.

2. Flexible energy storage devices

SCs, also regarded as electrochemical capacitors, are mainly divided into two categories based on the energy storage mechanism: electrical double layer capacitors (EDLCs) and pseudo-supercapacitors [13,27]. The capacitance of an EDLC is mainly derived from the charge separation and accumulation at the electrode/electrolyte interface (Fig. 2(a)) [28]. Consequently, both the accessible surface features and pore size distribution of electrode materials would influence the capacity of an EDLC. Owing to the easy accessibility, simple processing, and high chemical stability, carbon materials including activated carbon, carbon nanotubes (CNTs) and graphene are usually extensively employed as electrode materials of EDLCs [29–31]. The physical process during charging/discharging endows EDLCs with high power density. However, the energy density of EDLCs is usually low due to the limited specific surface area of electrode materials in the process of electrochemical contact with electrolyte [32]. Differently, pseudo-capacitive active materials, such as conducting polymers and transition metal oxides, generate pseudo-capacitance from the reversible Faradaic reactions, resulting in relatively high energy density. Nevertheless, their low conductivity leads to low power density. Therefore, the incorporation of pseudo-capacitive materials into carbon architectures is desired to improve the overall performance of the SC electrodes.

Compared with SCs, LIBs generally possess higher energy density [7,35]. A conventional LIB often uses carbon material and lithium-metal oxide as anode and cathode, respectively, in which lithium ions reversibly extract and insert between two electrodes along with the removal and addition of electrons (Fig. 2(b)). With an analogous reaction mechanism to LIBs, sodium-ion batteries (SIBs) are receiving considerable attention and have been regarded as one of the most prospective alternatives for energy storage due to the low cost and abundant resources of sodium [36]. However, the energy density for both batteries is far from the requirements of mobile electronic devices despite that the energy density of insertion-type LIBs has reached nearly to their theoretical value. Compared to the cathodes of LIBs or SIBs with a single-ion-intercalation reaction mechanism, whose capacities are less than 250 mAh g^{-1} [37], S and O_2 based on multi-ion conversion

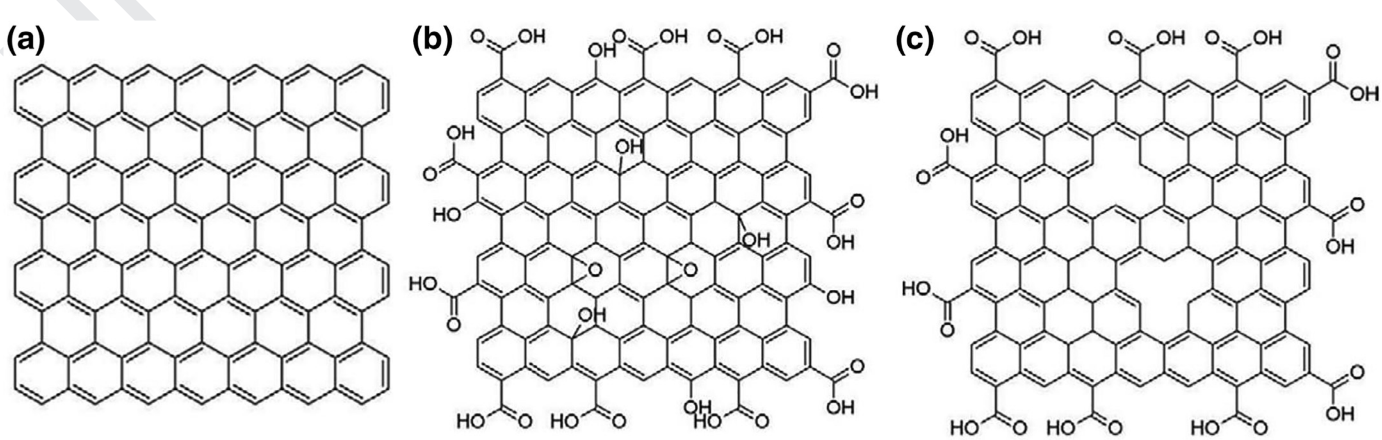

Fig. 1. Structural models of (a) graphene, (b) graphene oxide (GO) and (c) reduced graphene oxide (RGO) [24].

Please cite this article as: K. Chen et al., Graphene-based materials for flexible energy storage devices, Journal of Energy Chemistry (2017), https://doi.org/10.1016/j.jechem.2017.08.015