ANNALS OF THE UNIVERSITY OF ORADEA
FASCICLE OF TEXTILES, LEATHERWORK

ADVANCES IN THE DEVELOPMENT OF TEXTILE SUPERCAPACITORS: MATERIALS, TECHNOLOGIES AND PRINCIPLES

MARIN Adrian[1], AILENI Raluca Maria[2], SÂRBU Teodor[3]

[1, 3] INCDTP, 030508, Bucharest, Romania, E-Mail: Adrian.marin@ incdtp.ro

Corresponding author: MARIN Adrian, E-mail: Adrian.marin@ incdtp.ro

Abstract: *The current context is marked by an increased demand for efficient and flexible energy storage solutions. Due to the increased interest in this field, researchers are focusing on developing supercapacitors integrated into textile materials. This innovation promises to revolutionize areas such as smart clothing and wearable electronics, combining the advantages of textile materials that exhibit high-performance supercapacitors in terms of the rapidity of the charging and discharging process. The choice of electrode materials, such as carbon, conductive polymers, and metal oxides, is necessary for optimizing the capacity, energy density, and cyclic stability of the supercapacitors integrated into textiles. By integrating supercapacitors into textile materials, new perspectives are opened for efficient energy management in the digital era, offering innovative solutions in powering wearable devices and improving the quality of life through sustainable technologies at a reduced cost. This research direction highlights the importance of continuously developing materials and manufacturing technologies to precisely meet the increasing energy requirements.*

Key words: *supercapacitors, textiles, methods, functionalization, conductive materials.*

1. INTRODUCTION

Developing improved energy storage devices is one of the keys to successful global energy management for a greener and more energy balanced environment. In particular, one of the challenges is to improve energy transportability: lighter, more compact and mechanically flexible energy storage devices are needed for a significant number of applications, from wearable energy that could be incorporated into clothing, to space applications where the cost per weight and volume is enormous.

A number of recent studies, initiatives and products have been reported and proposed for the development of flexible energy devices based on various types such as Zn-MnO_2 (non-rechargeable) primary batteries, Li-MnO2 primary batteries as well as secondary batteries (rechargeable) such as lithium batteries, supercapacitors or systems based on radical polymers [1].

The increasing demand for energy and, at the same time, the depletion of natural resources are factors of a sustainable form of energy and storage since the second half of the 20th century. Harvesting renewable forms of energy, such as solar energy, wind energy, tidal energy, etc. are some examples that are being researched for indoor/outdoor applications from wearables to robots and grid power. One of the challenges for renewables is that they provide intermittent power, and as a result, environmentally friendly energy storage devices such as batteries and supercapacitors (SCs) are required. The launch of lithium-ion batteries in portable devices by Sony Corporation in the early 1990s was a major shift in technological advancements in electronic gadgets such as mobile phones, wearables, robots and autonomous devices, electric vehicles, etc. Supercapacitors or ultracapacitors are considered among the most efficient electrochemical energy storage devices because they offer high capacity, excellent energy density and specific power, high stability at charge-discharge rates, longer lifetime, and another aspect is represented by the fact that they can be light, flexible and portable. Compared to battery devices, supercapacitors offer higher energy density, longer cycling stability and faster charge-discharge process [2].

2. HISTORY OF SUPERCAPACITORS

There are many types of methods and elements that can be used for energy storage, where capacitors are one of the fundamental electrical circuit elements. From the simplest electrostatic capacitors to electrolytic capacitors, and then to supercapacitors, capacitance has been increased from milli-farads (mf) to hundreds or even thousands of farads (f), and the efficiency and effectiveness of capacitors have also been improved.

The first supercapacitor was the leyden jar. In 1746, Pieter Van Musschenbroek made a double-layer supercapacitor in Leyden in the Netherlands. It was found that electric charges could be stored on plates in the configuration, and the so-called capacitor was connected with a capacitor in the electrostatic mechanism. However, the first patent was not registered until 1957, when a carbon-based capacitor with a large surface area was illustrated. The electrolytic capacitor was then developed and commercialised as a polarised capacitor in which the conductive salts of the electrolyte interact with the metal electrodes. Basically, two metal sheets coated with a layer of insulating oxide were placed with a paper separator soaked with electrolyte. The thin oxide layers on the electrodes acted as dielectric elements, giving a higher capacitance per unit volume compared to electrostatic capacitors. Aluminium, tantalum, niobium and niobium oxides were commonly used to make electrolytic capacitors, with relative permittivity ranging from 9.6 to 41, and capacitivity ranging from a few µf to tens of mf, or even in some extreme cases, hundreds of mf [1,3]. Compared to traditional electrostatic and electrolytic capacitors, supercapacitors offer tens to hundreds of times more specific energy. In addition, supercapacitors can deliver higher specific power than many types of batteries, while the specific energy of supercapacitors is relatively lower than that of batteries.

Supercapacitors are the key to closing the gap between the two energy storage devices, batteries and capacitors, and establishing energy storage devices that charge fast and provide intermediate specific energy. Because their charge storage process is highly reversible, supercapacitors have relatively longer life cycles and can exhibit fast responses in both charging and discharging. This has led to considerable interest in their applications in various consumer electronic devices, industrial energy management systems and hybrid electric and fossil fuel vehicles [2,3].

2.1 Fundamental principles

Supercapacitors, also known as ultracapacitors or electrochemical capacitors [4,11], stand out in the energy storage landscape because of their unique mechanism for storing electrical energy. Unlike batteries, which rely on chemical reactions to store and release energy [5], supercapacitors store energy by physically separating charge in an electric double layer (EDL).This fundamental difference gives supercapacitors fast charge and discharge capabilities, exceptional power density and a lifetime that far exceeds that of conventional batteries [6]. Energy storage in supercapacitors is facilitated primarily by two mechanisms: electrical double layer capacitance (EDLC) and Pseudocapacitance. EDLC occurs at the interface between the electrode surface and the electrolyte, where a charge separation is formed with no real electron transfer across the interface, similar to a parallel plate capacitor [7,13]. This phenomenon is predominantly observed in carbon-based electrodes, where the large surface area and porous structure provide an extended interface for charge accumulation [8]. The performance of supercapacitors is governed by several key parameters, with capacitance, energy density, power density and cyclic stability emerging as critical factors. Capacitance, measured in farads (F), indicates the amount of charge a supercapacitor can store at a given voltage. It is intrinsically related to the electrode surface area and the distance between the electrode and the electrolyte ions. The choice of electrode material and its nanostructure is essential in defining the characteristics of the supercapacitor. Materials with large surface areas, such as activated carbon, graphene and carbon nanotubes, are preferred for EDLC supercapacitors [9]. For pseudocapacitive supercapacitors, materials that undergo redox reactions, such as certain metal oxides (e.g. RuO_2, MnO_2) and conductive polymers (e.g. polyaniline, polypyrrole) are chosen [8]. Figure 1 shows types of flexible supercapacitors and their typical configurations.

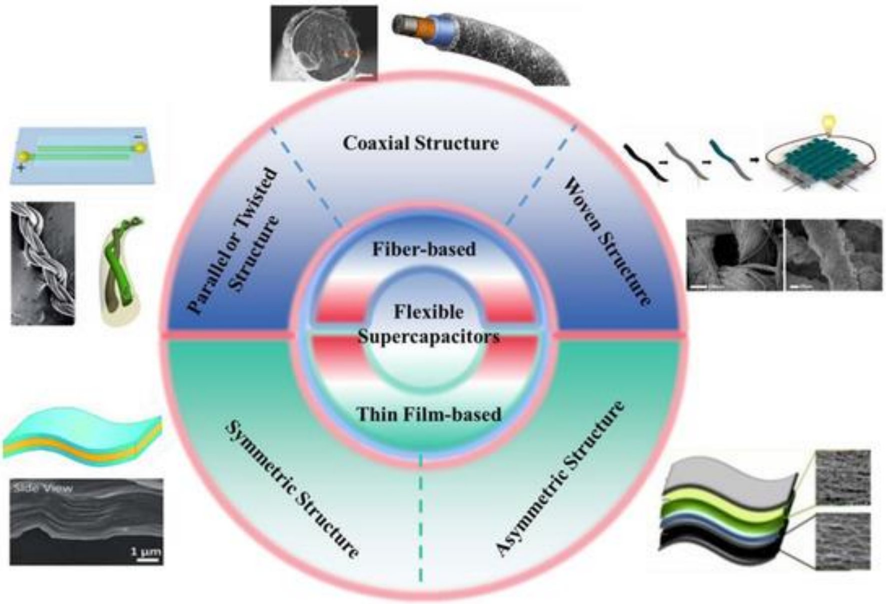

Fig. 1. *Flexible supercapacitors and their typical configurations [10].*

2.2 Classification of supercapacitors

Supercapacitors are divided into three different categories, as shown in Figure 2, where they are classified according to their charging mechanisms: (a) double-layer capacitors; (b) pseudocapacitors; and (c) hybrid capacitors.

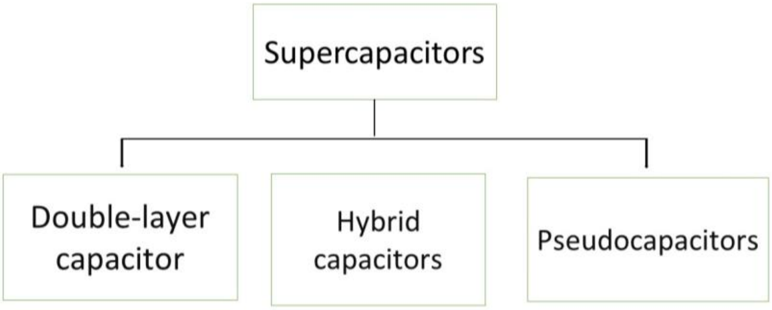

Fig.2. *Classification of Supercapacitors [13]*

In the case of double-layer capacitors, an energy storage system is formed containing two layers of polarising electrodes, placed between a separator and charged with electrolytes. Energy can be stored as an electrostatic mechanism.

Pseudocapacitors energy is stored via the reduction-oxidation (redox) material in the context of redox reactions, where the fast chemical reaction serves as a capacitance.

For hybrid supercapacitors, substances such as activated carbon, conducting polymers or even transition metal oxides are doped or added to the electrodes so that supercapacitors can exhibit both electrostatic responses and reversible Faradaic charge transfer, where the lithium ion supercapacitor is a typical example in this category [1].

2.3 Energy storage mechanism in supercapacitors

In general, two different operating principles are applied for energy storage in supercapacitors: (1) double-layered capacitance, or so-called electrical/electrochemical double-layered capacitance (EDLC), and (2) pseudocapacitance [1].

Electrical double layer capacitance (EDLC)

In double-layered capacitance, energy is stored in a manner similar to that of a traditional parallel capacitor by separating charges. However, it can retain a much larger amount of energy than a conventional capacitor. Since charge separation occurs over a relatively small distance in the case of an electric double layer, the interface can be established between a particular electrode and its adjacent electrolyte [1,2].

Pseudo-capacity

In pseudocapacitance, a relatively large capacitance is found under a non-electrostatic base, which is due to a reversible Faradaic charge transfer. In addition, with a limited amount of active material or effective surface area, a capacitance related to an electrochemical charge transfer process is produced. Recently, pseudocapacitive materials investigated are transition metal oxides such as manganese(II) oxide (MnO_2), and conducting polymers such as polypyrroles (Ppy), polyaniline (PAni) or polythiophene (PTh) derivatives (e.g. poly(3,4-ethylenedioxythiophene), PEDOT)[1].

3. ELECTRODE MATERIALS

Supercapacitors can be made from a wide range of materials, such as carbon materials, conducting polymers and metal oxides, with the selection of the material used depending on the type of capacitance, specifically the storage mechanism to be used. For double-layered capacitance, carbonaceous materials are generally used, and for pseudocapacitance, metal oxides and conductive polymers are commonly applied. Therefore, for capacitors exhibiting both types of capacitance, either carbon composite materials with metal oxides or conductive polymers are used [1].

4. SUPERCAPACITORS BASED ON COATED TEXTILES

Since many textiles or fabrics are not conductive (e.g. cotton, wool, nylon, polyester), before applying these substrates to prepare flexible textile-based supercapacitors, their electrical conductivity must be improved. To facilitate better electrical conduction on various non-conductive fabric surfaces, a layer of conductive material is usually applied to the surfaces of yarns or fibres. This conductive layer can be prepared by physical vapour deposition (PVD), chemical vapour deposition (CVD), electrostatic spraying, electroless deposition, solution casting, dip coating or simply screen printing.

Various types of textile materials, including cotton, polyester, polyamide, spandex and carbon fabrics, are widely used to produce supercapacitors, and research results have been reported. Researchers have developed flexible electrodes with a PANI-CNT-Cotton combination with a specific capacitance of 410 Fg^{-1}. After 3000 cycles, it degraded to 61% of its original value[7]. Then, other researchers further developed this idea and developed another flexible PANI-CNT-Cotton/Polyester electrode with a specific capacitance and areal capacitance of 11.1 Fg-1. After cycling this test device more than 15,000 times, 95% of the original capacitance could be maintained[8]. In another paper, it was reported how a stretchable textile was fabricated by direct immersion of a Spandex fabric substrate in an aqueous PEDOT-PSS dispersion. An average conductivity of 0.1 $S/cm-^{1}$ was measured from this conductive fabric, and by repeating the immersion step, the conductivity of the fabric increased to 2.0 S/cm^{-1} and gave a 33% faster switching speed[1]. In another study, polypyrrole/lignosulphonate (PPy/LGS) was deposited on cotton fabrics by *in situ* chemical oxidative polymerization of pyrrole in the presence of lignosulphonate, which functioned as both a template and a dopant. The electrical conductivity of the fabric increased to 3.03 S/cm^{-1} [9].

5. CONCLUSIONS

Sustainability and energy self-sufficiency are important aspects of the green economy. In this regard, this review article summarizes recent advances and various synthetic procedures used for the development of various flexible electrodes. Innovative materials such as metal oxides, conductive polymers and carbonaceous materials, together with advanced fabrication methods, suport the development of textile supercapacitors with improved conductivity capabilities, offering a promising approach to meeting energy requirements.

REFERENCES

[1]. C. Hui, C. Kan, C. Mak, K. Chau, Flexible Energy Storage System—An Introductory Review of Textile-Based Flexible Supercapacitors, Processes 7 (2019) 922.

[2]. P. Forouzandeh, P. Ganguly, R. Dahiya, S.C. Pillai, Supercapacitor electrode fabrication through chemical and physical routes, J Power Sources 519 (2022) 230744.

[3]. Z.Y.D.N.A.Z. and B.Z.J. Chenguang Liu, Graphene-Based Supercapacitor with an Ultrahigh Energy Density, (n.d.).

[4]. R. Kötz, M. Carlen, Principles and applications of electrochemical capacitors,

Electrochim Acta 45 (2000) 2483–2498.

[5]. P. Simon, Y. Gogotsi, Materials for electrochemical capacitors, Nat Mater 7 (2008) 845–854.

[6]. L.L. Zhang, X.S. Zhao, Carbon-based materials as supercapacitor electrodes, Chem Soc Rev 38 (2009) 2520.

[7] .Yong, S.; Owen, J.R.; Tudor, M.J.; Beeby, S.P. Fabric based supercapacitor. J. Phys. Conf. Ser. 2013, 476, 012114.

[8]. Ding, Y.; Invernale, M.A.; Sotzing, G.A. Conductivity trends of PEDOT-PSS impregnated fabric and the effect of conductivity on electrochromic textile. ACS Appl. Mater. Interfaces 2010, 2, 1588–1593.

[9]. L. Zhu, L. Wu, Y. Sun, M. Li, J. Xu, Z. Bai, G. Liang, L. Liu, D. Fang, W. Xu, Cotton fabrics coated with lignosulfonate-doped polypyrrole for flexible supercapacitor electrodes, RSC Adv 4 (2014) 6261.

[10]. P. Teymoory, J. Zhao, C. Shen, How Practical Are Fiber Supercapacitors for Wearable Energy Storage Applications?, Micromachines (Basel) 14 (2023) 1249.

[11]. Chu, Andrew, and P. O. Braatz. "Comparison of Commercial Supercapacitors and High-power Lithium-ion Batteries for Power-assist Applications in Hybrid Electric Vehicles I. Initial Characterization." Journal of Power Sources, 2002,

[12]. Dong, Zhipeng, and Jing Guo. "On Low-Resistance Contacts to 2-D MoTe₂ by Crystalline Phase Junctions." IEEE Transactions on Electron Devices, 2018.

[13]. Subramanian, A., Balraj, B., & Easwaramoorthy, N. (2021). Nanotechnology for Electrical Energy Systems: Studies on the Energy Storage Capabilities and Energy Utilization Efficiency of Nanomaterials. In Handbook of Nanomaterials and Nanocomposites for Energy and Environmental Applications (pp. 1679-1701). Cham: Springer International Publishing.