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Last developments in polymers for wearable energy storage devices

Silvia Lage-Rivera | **Ana Ares-Pernas** | **María-José Abad**

Universidade da Coruña, Campus Industrial de Ferrol, Grupo de Polímeros-CIT, Campus de Esteiro, Ferrol, Spain

Correspondence
María-José Abad, Universidade da Coruña, Campus Industrial de Ferrol, Grupo de Polímeros-CIT, Campus de Esteiro, Ferrol 15403, Spain.
Email: maria.jose.abad@udc.es

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Summary

Our modern and technological society requests enhanced energy storage devices to tackle the current necessities. In addition, wearable electronic devices are being demanding because they offer many facilities to the person wearing it. In this manuscript, a historical review is made about the available energy storage devices focusing on super-capacitors and lithium-ion batteries, since they currently are the most present in the industry, and the possible polymeric materials suitable on wearable energy storage devices. Polymers are a suitable option because they not only possess remarkable mechanical resistance, flexibility, long life-times, easy manufacturing techniques and low cost in addition to they can be environmentally friendly, nontoxic, and even biodegradable too. Moreover, the electrical and electrochemical polymer properties can be tunning with suitable fillers giving to versatile conducting polymer composites with a good cost and properties' ratio. Although the advances are promising, there are still many drawbacks that need to be overcome. Future research should focus on improving both the performance of materials and their processability on an industrial scale, where additive manufacturing offers many possibilities. The sustainability of new energy storage devices should not

Abbreviations: 1D, one dimension; 3D, three dimensions; A, area of the electrode applied; AM, additive manufacturing; C, capacitance; CB, carbon black; CF, carbon fibers; CFO, cobalt ferrite; CNF, carbon nano fibers; CNT, carbon nano tubes; CPC, conductive polymer composites; D, dielectric displacement; d, thickness of dielectric layer; DEA, dielectric thermal analysis; DLP, digital light processing; E, applied electric field; E_b, breakdown strength; EBM, electron beam melting; ECNF, electrospun carbon nanofibers; EDLC, electrochemical double layer capacitor; EH, energy harvesting; F, Farad; FDM, fusion deposition modelling; GN, graphene nanosheets; GO, graphene oxide; HN-CNF, N-doped carbon nanofibers; ICP, intrinsically conducting polymers; IoT, internet of things; LDM, liquid deposition modeling; LFP, lithium iron phosphate; LIB, lithium-ion batteries; LMO, lithium manganese oxide; LTO, lithium titanate oxide; MABs, metal-air batteries; MWCNT, multi-walled carbon nanotubes; PANI, polyaniline; PDA, polydopamine; PEDOT:PSS, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate; PEG, poly ethylene glycol; PEO, polyethylene glycol; PET, poly ethylene terephthalate; PHBV, poly(hydroxy butyrate-co-hydroxyvalerate); PI, polyimide; PLA, poly lactic acid; PMMA, poly methyl methacrylate; PPY, polypyrrole; PTPA, poly tri-phenyl amine; PVA, polyvinyl acetate; PVDF, poly vinylidene fluoride; PVDF-HFP, poly (vinylidene fluoride)-co-hexafluoropropylene; PVP, poly vinyl pyrrolidone; PZT, lead zirconate titanate; QD, quantum dots; RF, radiofrequency; rGO, reduced graphene oxide; SC, super-capacitors; SLA, stereolithography; SLS, selective laser sintering; SWCNT, single walled carbon nano tubes; t, discharge time; TRGO, thermally reduced graphene oxide; T-ZnOw, tetra-pod zinc whiskers; U_e, energy density; ε_0, dielectric permittivity of vacuum (8854×10^{-15} F cm^{-1}); ε_r, dielectric permittivity.

be forgotten, encouraging the use of more environmentally friendly materials and manufacturing processes.

KEYWORDS

batteries, energy storage, polymer composites, super-capacitors, wearable

1 | INTRODUCTION OF ENERGY STORAGE DEVICES AND POLYMER COMPOSITES IMPLEMENTATION IN THEIR MANUFACTURE

1.1 | The need of energy storage devices

Over the last few decades, humanity is going through a technological change for the sake of reaching the information era, in which more and more electronic devices are needed. In addition, the industry 4.0 is attempting to make factories more intelligent by introducing all their machines and processes interconnected, which requires a considerable number of electronic devices connected by internet of things (IoT).

Some of these electronics are being increasingly demanded by ordinary people,[1] who take them as wearable electronics[2] and sensors.[3-5] Textile industry is already designing fashionable electronic devices that can be worn as accessories (smart watches, necklaces, earrings, etc.) and clothes.[6] For example, Li et al[7] reported a wearable and flexible pressure sensor, very useful in health care monitoring. This kind of portable devices need flexible and lightweight materials.

Some of them require low power incoming (0.1-10 mW) and thus they can be fed with energy harvesting (EH) devices.[8-10] EH (Figure 1) is a clean energy obtaining method which uses wasted energy that is free in the environment. However, the electrical power harvested through these technologies has interruptions in their generation so, in most applications, it is desirable to couple an energy storage unit compatible with the device. Energy production and storage can be achieved thanks to multifunctional materials, which are able to develop various tasks (energy storage and harvesting) in an efficient way.[11,12]

Taking a historical review, electronic devices have been powered by rechargeable batteries since Gaston Planté invented the first one based on acid and lead in 1859[13] (Figure 2A). This technology faces several disadvantages such as their limited lifetime caused by the heating up and down that the battery suffers when the

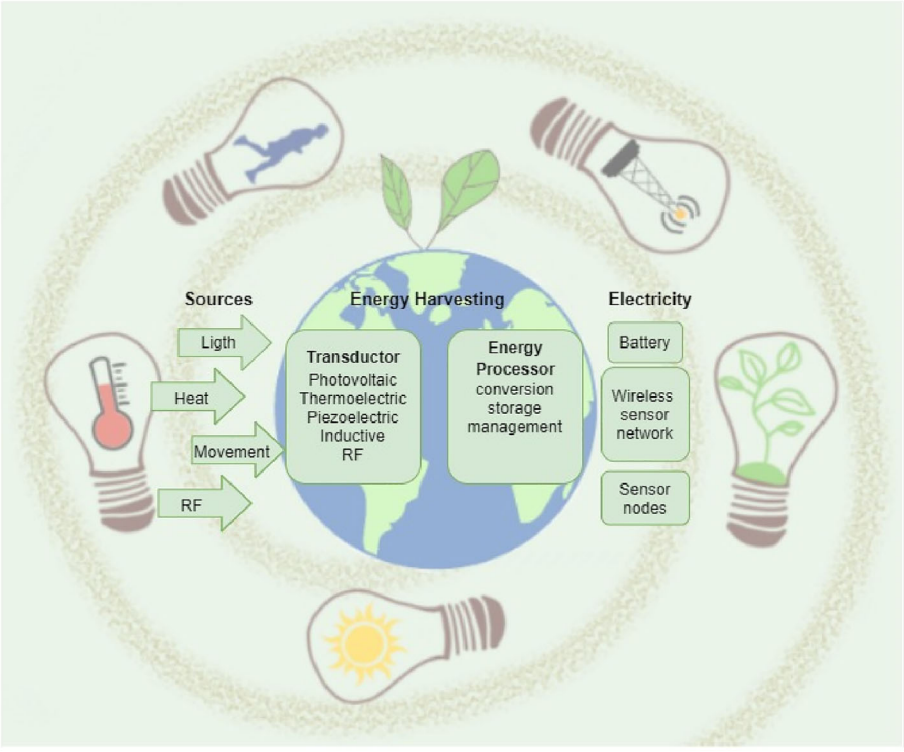


FIGURE 1 Energy harvesting

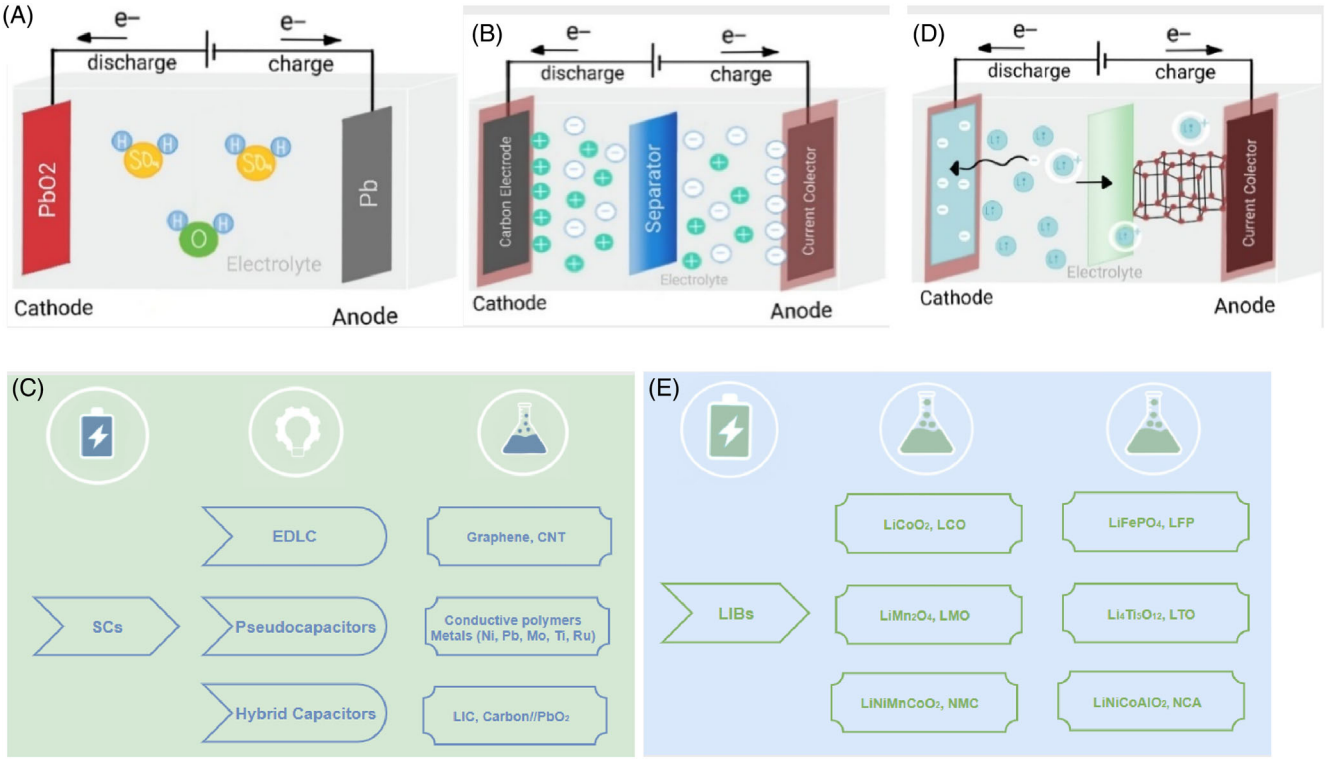


FIGURE 2 Schemes of (A) lead acid battery (B) SC (C) SC technologies and principal materials (D) LIB (E) LIB cathodes materials. LIB, lithium-ion batteries; SC, super-capacitors

ions flow back and forward, or the environmental contamination because of their chemical components in the cathode and anode. Scientists are trying to overcome with these difficulties hence, new studies are appearing looking for materials with high power and energy density properties as an alternative to common batteries. In 1878, Maiche discovered the metal-air batteries (MABs),[14] which seemed like a good lead-acid alternative. MABs are composed of an air-breathing cathode (which catches oxygen from the air), a metal anode (zinc,[15] lithium,[16] sodium, potassium, and more) and an electrolyte, which can be aqueous or nonaqueous. MABs can be assembled in several forms (solid-state,[17] fiber-type,[18] etc) to cover a wide range of applications. Despite the great advantages of MABs, such as their remarkable density (3-30 times higher than lithium-ion batteries [LIB]) or high level of safety, they face several disadvantages as their lack of scalability for industrial development, and the need of more suitable and enhanced materials compose them.[18,19] However, scientists are trying to overcome these drawbacks[20] and hopefully MABs will be present in our future electronic devices. Nowadays, the storage devices that are most available in the industry are super-capacitors (SC) and LIB because of their mechanical robustness and electrochemical sustainability[21] so, this review is focused those two technologies.

The use of polymers and polymer composites in the fabrication of energy storage devices has been investigated[21] because of its multiple advantages over inorganic materials. A polymer material is obtained by a polymerization process, in which a lot of molecules (called monomers) are linked to each other by covalent bonds. They seem a good alternative to the typical inorganic ones used so far in energy storage devices because of their intrinsically physical properties.[22] They are flexible, resistant, tailorable, lightweight, easy to process, and they have lower cost than inorganic ones. Polymers possess some intrinsic physical properties (viscoelasticity, glass transition temperature, etc.) which make them unique and very useful in several applications. Moreover, the use of bio-based polymers[23,24] can help with the current ecological challenges. Biopolymers are obtained from natural sources, they are non-oil dependent, nontoxic, they help with the current ecological challenges, and they are biodegradable under certain conditions, which make them discard easily.

For the manufacture of energy storage devices, polymeric materials must have certain electrical properties. The most commonly used are intrinsically conducting polymers (ICP), generally with poor mechanical properties, and conductive polymer composites, where an electrical insulant matrix is added with conductive fillers.

These synergistic combinations allow optimization of both mechanical and electrical properties, impossible to achieve from each component alone.

The main target of this comprehensive review is to explain the principal energy storage devices industrially available and review the advances in the design and performance of these energy storage devices obtained using ICP and conducting polymer composites. Therefore, it is going to focus on new developments for wearable LIB and SC, where the implementation of polymeric materials is essential to achieve the desired properties.

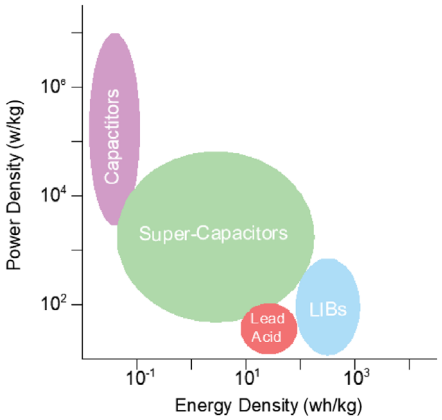


FIGURE 3 Ragone plot

1.2 | Super-capacitors

The most studied alternative to lead-acid batteries has been SC, discovered in 1957 by General Electric's H.I. Becker.[13] SC are a kind of capacitors with a high capacitance, which makes SC able to store energy. In these devices, the energy is stored electrostatically within the carbon pores at the electrodes surface area, so the capacitance and consequently the energy density increase with the controlled porosity.[25] This results in the increase of speed in charge and discharge cycles (1-10 seconds[26]) but it also produces a reduction in their lifetime. However, SC possess a high lifetime because they do not need chemical reactions to store the energy (around 10^5 charge/discharge cycles[27]).

SC are mainly composed by two identical electrodes acting as anode and cathode based on porous materials, normally carbonaceous (activated carbon, graphite,[28] ICP and others), on account of their high capacitances (up to 394 F g^{-1})[29] and large surface areas. They also possess an active layer, a separator for avoiding short-circuits between the anode and cathode, and the current collectors (Figure 2B).

Unlike capacitors, which are composed by two plates with a dielectric inside as an insulator, SC have an electrolyte as insulated active layer. Therefore, the distance between their plates can be significantly smaller than in capacitors. The electrolyte is usually liquid, made by metal salt solution with organic or aqueous materials as solvent. Some investigations propose to use dielectric polymers as SC electrolytes because they avoid the need of a separately separator.[12,30]

There are three types of SC; electrochemical double layer capacitor (EDLC), pseudo-capacitors, and hybrid capacitors, Figure 2C summarizes the most used materials in each one. The charge storage mechanism and the electrodes capacitance change in each of them:

- *EDLCs* were the first SC discovered when Standard Oil Co. (1966) was doing experiments with porous carbon material as electrodes, and they realized that the energy was stored in the carbon pores. They are mostly made with carbonaceous materials due to their high specific surface area, which electrostatically store the charge at the interface between the electrode and the electrolyte.[31] EDLC can be easily disposable and burnable avoiding high costs in their discarding and recycling. Nowadays, they are still the most used ones due to their technical development.
  EDLC main problems are their low energy density due to their low capacity. Muralee Gopi et al[26] proposed to use surface modification methods (N- and S-doping, surface exfoliation, and surface activation) to overcome these drawbacks.
  From another point of view, Liu et al[32] focused their study on ways to avoid SC self-discharge to improve SC technology. This improvement can be obtained by tuning the separator, making modifications on the electrodes, or modulating the electrolyte.
- *Pseudo-capacitors* do not store the charge electrostatically but electrochemically with reversible surface (or near-surface) Faradaic redox reactions, this means the involving of charge transfer reactions throughout the electrochemical interface. They owe their name to their kinetic and thermodynamic behavior which can be explained with the mathematical model for surface adsorption and desorption.[33] Their electrodes could be made with transition metal oxides or conducting polymers.[31,34] Despite their lower specific power density and stability in comparison with EDLC, their specific capacitance is high. However, pseudo-capacitors lose capacity faster than EDLC do because of the electrostatic stresses that they suffer in charge and discharge processes.
- The *Hybrid SC* are composed by a combination of EDLC and pseudo-capacitor leading to high energy densities and high capacitances.[26] New developments

are appearing in the hybrid SC field as lithium-ion capacitors,[35] which possess high power and energy density.

Compared to current batteries, SC do not suffer from explosion, so they gain on security. Moreover, they do not need toxic chemical materials to work, making them environmental-friendly and easy to recycle. Besides, SC are smaller than lead acid batteries and they can be charged and discharge thousands of times very quickly, as a result, new applications arise.

The Ragone plot[36] (Figure 3) summarizes the energy and power densities of the different energy storage devices. Despite current SC do not possess high energy density, they have the highest power densities making them suitable in current stabilization applications (variable voltage). That is the reason why SC are very used in electronic (power supply circuits, computers, inverters, cameras, etc.), energy production (wind and solar energy), and transportation devices. Moreover, scientists are attempting to enhance SC' energy densities improving the electrodes performance by adding novel 2D material such as MXenes,[25] metal-organic frameworks[37] or by functionalization with thiol.[38]

In addition, SC are now an essential component in the development of renewable energy devices because they can support intermittent input energy. Also, the electrical vehicle industry has an eye on this technology on account of their short charge rates, long lifetime, and small volume making them suitable for fast recharging vehicles used in short-frequent trips.[39] Several researchers have recently published advances in SC technology for vehicle applications,[40,41] some of them combine super capacitors with other batteries gaining better performances.[42-45]

SC are also being used in wearable and portable energy storage devices.[46-48] The investigation reported in this field always attempt to enhance the energy density, flexibility, and tailorability. Polymer-based materials can provide these properties.[49] Wang et al[50] recently stated last advances in polymer materials for electrodes and electrolytes in SC which can be used in wearable applications.

1.3 | Lithium-ion batteries

During the oil crisis in 1970 decade, Stanley Whittingham (2019 Nobel Prize) discovered LIB thanks to some experiments consisting of holding lithium ions between titanium sulfite plates. Although, he did not pay much more attention to the technology and it was not until 1991 that Sony and Ashai Kasei developed the first commercial LIB.[13]

The most outstanding LIB' characteristic is their energy density because they exceed the values of both Lead-Acid batteries and SC. Regarding the efficiency, LIB can achieve a 92% vs the 60% of traditional batteries, considering the efficiency as the rate charge/discharge density. The last remarkable advantage of LIB is their security. LIB do not explode because they have control systems to protect them from overcharges. By contrast, the cost of LIB is higher than Lead-Acid ones, but this parameter is decreasing in recent years.

The main parts of LIB are the cathode, anode, electrolyte, separator, and current collectors (Figure 2D). Energy storage occurs by some electrochemical redox reactions between the anode and the cathode electrodes composed by a range of electrochemically active materials. Traditional LIB has a Lithium cathode, due to its high electrochemical capacity and a carbonaceous material anode (activated carbon, carbon black, graphene, etc.).[51]

Figure 2E collects possible LIB cathode materials,[52] all of them contain lithium. This material possesses a high reactivity (even with the water) so, there is no need of complex chemicals as electrolyte. The aforementioned reactivity also allows them to store a lot of energy in its atomic bonds, resulting in higher energy density in a lower volume.[53]

The most common LIB' anodes are the graphite oxide ones because they support very well the volume changes that LIB suffer. However, graphite anodes have low capacities (372 mAh g^{-1}) and their rates of performance (capacity over number of cycles) are poor so new materials are being investigated to replace them.[54] Other carbonaceous materials (carbon nano fibers [CNF], carbon composites, biomass carbon, mesoporous carbon, etc.) are a suitable option because they help the lithium diffusivity and electrons movement between electrode and electrolyte. Another anode material could be the silicon, because of its high theoretical specific capacity, low cost, and abundance in nature.[55] However, silicon has issues supporting the volume changes that the cell suffers.

The main purpose of the electrolyte is allowing the correct movement of lithium ions while the separator prevents short-circuit. However, the motion of ions carries degradation problems on the separator and the electrolyte so, new alternatives to traditional electrolytes are needed.[56] Chen et al[57] have recently noted the last progresses of solid-state electrolytes which reduce the degradation issue. From a different angle, some studies are focused on polymer composite electrolytes[58,59] because they avoid the need of the separator.

LIB is mainly used in portable electronics, such as smartphones, due to their high energy density (see Ragone plot in Figure 3), but they are also used in vehicle and industrial applications.[37] They can even be used for ultrafast charging and discharging applications.

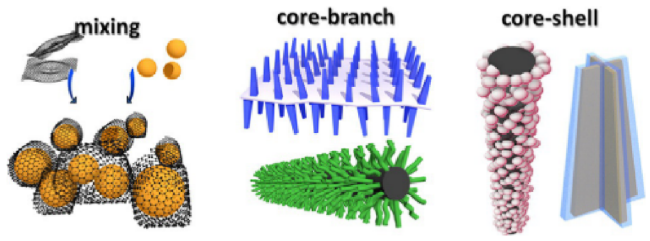


FIGURE 4 Main structure solutions of wearable batteries (Reference: 62. Reproduced with permission. Copyright 2015, Wiley-VCH)

Nevertheless, traditional LIB shows difficulties in wearable devices due to their lack of flexibility and adaptability to the human body because of their rigid plates as energy collector, currently made with copper and aluminum. To overcome this drawback, scientists are looking for new flexible and adaptable materials with enough electrochemical response to be used in LIB fabrication.[60] To achieve this goal, researchers have used polymer composites,[56,61] always searching for competitive electrical conductivities, electrochemical properties, and high mechanical strengths. Their work focuses on using a polymer or a polymer composite as electrode and then adding the anode/cathode substances, the most used ones are lithium titanate oxide (LTO)/lithium iron phosphate (LFP) and LTO/lithium manganese oxide (LMO). Once the electrodes are ready it is only necessary to add the electrolyte to get the LIB. Another field for LIB improvement is the study of new electrolyte materials because new requirements on their properties are needed like being environmentally-friendly and low-cost. Focusing on the physical properties, they must possess a high ionic conductivity, wide potential window, high thermal, chemical, and electrochemical stability, and be inert to the other LIB parts.

In both SC and LIB electrodes is important not only the nature of their materials but also its microstructure. The most common structures in energy storage devices can be obtained by three methods, mixing type, core-branch and core-shell (Figure 4). Zhu et al[63] reported in 2015 the electrodes microstructure design and they confirmed the advantages of two materials composed electrodes.

Researchers are also worried about LIB security because the portable devices are really close to the human body. Chen et al[64] recently reviewed the most important investigations about the electrical, thermal,[65] and mechanical issues in LIB. Once these safety concerns are solved, new applications for LIB will appear.

Table 1 compares the principal energy storage properties of lead-acid batteries, SC and LIB in order to see the strengths of each technology. There are also data of the newest and improved technologies.

1.4 | Required physical properties on the polymer composites for energy storage

To improve the performance of batteries, the research is focused on increasing the specific physical properties of the polymer composites from which they are made. The main parameters required for studying and comparing electrochemical cell performance are both energy and power densities.

The energy density is the amount of charge that a battery can store whereas the power density is the quantity of energy that the battery can discharge, both parameters regarding its mass. A battery with high energy density provides energy in a lower volume, which means reducing its cost and footprint. In addition, a battery with high power-deliver capability is suitable in applications where high power peaks are required.

The maximum volumetric energy density depends on the applied electric field as it is shown in Equation (1). Simultaneously, Equation (2) collects the relation between the dielectric displacement in linear dielectrics and the applied field. Solving the Equations (1) and (2), Equation (3) shows the maximum energy density that a linear dielectric material can store. Therefore, it depends on the dielectric parameters of the material because it is related to the relative dielectric permittivity and to the dielectric breakdown strength.[68]

$$U_e = \int_0^{D_m} E\, dD. \tag{1}$$

$$D = \varepsilon_0 \cdot \varepsilon_r \cdot E. \tag{2}$$

$$U_e = \int_0^{D_m} \frac{D}{\varepsilon_0 \cdot \varepsilon_r} dD = \frac{1}{2} \cdot \varepsilon_r \cdot \varepsilon_0 \cdot {E_b}^2. \tag{3}$$

The dielectric breakdown strength is the most extreme electrical potential that a material can oppose before the electrical flow gets through the material. Both electric breakdown and dielectric permittivity can be easily measured in a laboratory.[68] Polymer dielectric permittivity[69] can be measured either directly with a DEA machine or by measuring the material capacitance, as shown in Equation (4).

$$\varepsilon_r = \frac{C \cdot d}{\varepsilon_0 \cdot A}. \tag{4}$$

Last, the power density relation with energy density is shown on Equation (5).

$$P_m = \frac{U_e}{t}. \tag{5}$$

TABLE 1 Comparison of the principal properties between the different energy storage technologies

Energy storage technology	Energy density (W h kg^{-1})	Power density (W kg^{-1})	Cycling stability	References
Lead-acid battery	25-35	150	50-100	66
Super-capacitors (SC)	100-150	10 000	>30 000	26,32
SC (graphene oxide scrolls)	206	32 000	>20 000	38
Lithium-ion batteries	100-250	500-2000	>500	26,33,55
Li-S	2600	—	—	67

Furthermore, parameters as the cycle life, charge/discharge characteristics, mechanical resistance, durability or degradation against external agents (like water, soaps or ultraviolet radiation) are measured to evaluate the future performance of the energy storage device.[50,70] Currently, there is a lack of high-performance polymeric electrode and electrolyte materials so new studies are emerging.[67,71,72]

Polymer composites are very often used in energy storage applications due their high dielectric permittivity and high dielectric breakdown strength.[30] However, there are some important factors such as the material additives, morphology, internal defects, and chemical impurities which affect the dielectric properties.

2 | POLYMER AND POLYMER COMPOSITES FOR BATTERIES OBTAINING AND THEIR VIABILITY FOR WEARABLE DEVICES

2.1 | Manufacturing methods of obtaining polymer-based batteries: additive manufacturing and electrospinning

The manufacture of more sustainable, efficient, and cheaper batteries is a key point in the development of greener energy technologies. One industrial scalable non-waste method very promising for battery obtaining is additive manufacturing (AM),[73] also known as 3D printing, due to their suitable characteristics like more freedom in design and low-cost feed materials. This method creates physical prototypes from virtual models in an easy process adding materials layer-by-layer. Nowadays, AM is being used in several fields such as bioscience, electronics, and energy storage[74] obtaining devices topologically optimized. Furthermore, AM technologies are becoming more affordable and accessible.

There are several AM processes, each of one is suitable for a different feed material and for different final applications (fusion deposition modelling [FDM], stereolithography [SLA], liquid deposition modeling [LDM], selective laser sintering, electron beam melting). However, the most used ones in energy storage devices are Fused Deposition Modeling and Liquid Deposition Modeling due to their scalability and their easy design method.[75] Both FDM and LDM are capable of printing macro- or micro- (even nano-) structures so different ones (fiber, cable, mesh, etc.) can be obtained.[76]

An alternative to AM technologies is electrospinning (Figure 5C), a widely used technique which obtains ultrafine polymer fibers with nano-sized diameters.[77] Electrospinning obtains nanofibers trough the coaxial stretching of a viscoelastic solution by applying a high voltage.[78] They possess a high area/mass ratio so they fit in energy storage devices as electrodes due to their ease in charge conduction mechanism.[61]

Following, the principal AM and electrospinning obtaining methods for batteries are explaining with some published investigations as examples. Table 2 collects capacity and electrical conductivity data of these studies to compare their electrical performance.

2.1.1 | Liquid deposition modeling

A huge amount of the 3D-printed LIB electrolytes[91,92] and electrodes[81] were obtained by LDM process, also known as direct ink writing.[93,94] The LDM method involves a syringe which prints the fed ink by a pneumatic system (Figure 5A). The inks are in a liquid state when they reach the nozzle and then they change to a solid-like state when the material exits the printer.

A big advantage of LDM is its capacity to print materials with a high loading of conductive fillers.[75] However, LDM technique requires post-processes like thermal annealing to solidify the final object and the layer resolution is limited.

Several researchers are looking for new polymer composites inks with suitable viscosity, which is an important property for this method. They are composed by active materials, fillers (organic as graphene oxide [GO] or inorganic as ceramic materials), and sometimes a polymer matrix (poly vinylidene fluoride [PVDF] mostly).

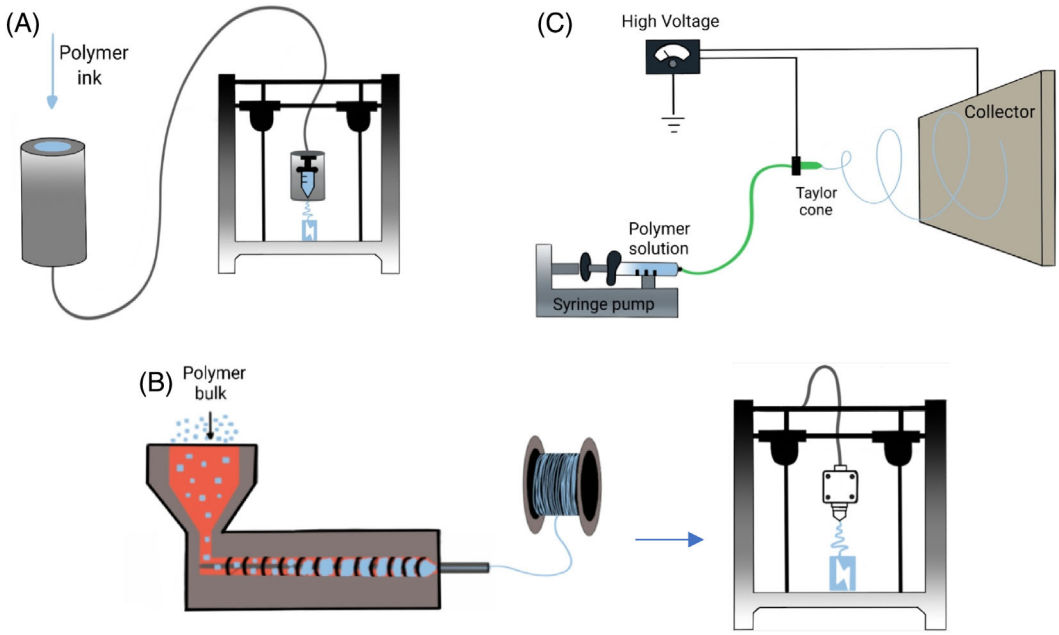


FIGURE 5 Manufacturing methods of obtaining polymer composites (A) liquid deposition modelling printing process (B) fusion deposition modeling printing process (C) electrospinning process

TABLE 2 Different examples of materials obtained by several manufacturing methods and their electrochemical properties

Materials	Composition	Flexible	Obtaining Method	Capacitance ($F\ g^{-1}$)	Conductivity ($S\ cm^{-1}$)	Uses	References
P(VDF-TrFE-CFE)	8:1:1	Yes	LDM	—	—	Binder	79
PVDF-HFP		No	LDM	—	3.8×10^{-3}	Battery separator	80
Commercial graphite slurry		No	LDM	1.3×10^{2}	—	Electrodes for LIB	81
Graphite/ $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$	Several	Yes	LDM	$(0.6\text{-}1.2) \times 10^{-2}$	(5-9)	Wearable LIB	82
(LFP/PLA)/(SiO_2/PLA)	6:4	No	FDM	1.11×10^{-3}	3.96×10^{-5}	Electrodes for LIB	83
L_{i2}TP/CB/PLA/ PEGDME500	4:4:1:1	No	FDM				84
PEO/LiTFSI	20:1	No	FDM	—	3.79×10^{-6}	Electrolyte for LIB	72
Graphene+active materials/PLA	4:6	No	FDM	—	—	Electrodes for SC and LIB	85
EGPEA/PANI-HCl/TPO	94.8:4.8:0.4	Yes	DLP	—	10^{-3}	SC	86
(AILCFN/NiCoS)/ AILCFN-3	—	Yes	Electrospinning	2.79×10^{3}	1.17×10^{1}	Electrodes for SC and LIB	87
PHBV/CFO	9:1	—	Electrospinning	$(3\text{–}4) \times 10^{-3}$	10^{-3}	Binder for LIB	88
PEDOT:PSS	94:6	Yes	Electrospinning	3.6	1.8	Electrodes for SC	89
HN-CNFs/GNs	98:2	Yes	Co-electrospinning	2.49×10^{2}	—	Electrodes for all-solid SC	90

Abbreviations: CB, carbon black; CFO, cobalt ferrite; DLP, digital light processing; FDM, fusion deposition modelling; GN, graphene nanosheets; HN-CNF, N-doped carbon nanofibers; LDM, liquid deposition modeling; LFP, lithium iron phosphate; PANI, polyaniline; PEO, polyethylene glycol; PLA, poly lactic acid; PVDF-HFP, poly (vinylidene fluoride)-co-hexafluoropropylene.

Joao et al[79] reported a terpolymer (which results from copolymeration of three monomers) called poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene) suitable for LDM processing to be used as a polymer binder for LIB. The terpolymer possess the needed rheological properties to be printed by LDM and it showed enhanced dielectric constant and low electric loss compared to the PVDF (one of the most common polymer binders in the current commercial batteries). In addition, this material could be a good option for wearable energy storage devices because of its flexibility. The same researchers' group[80] announced a strategy to print by LDM poly

(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP) copolymer, trying different infill densities and evaporation temperatures. They obtained remarkable cycling stability with 100% of infill density which is desirable in binders. These two options seem useful in those energy storage devices which do not possess a polymer electrolyte and therefore, they need a binder to ensure its correct operation.

Regarding the electrodes, on the one hand Zhang et al reported a method to obtain LDM printed ones with commercial graphite slurry.[81] They obtained remarkable capacity values in comparison with traditional electrodes used in LIB. This material is not flexible so it cannot be used in wearable devices. On the other hand, Praveen et al recently reported a yarn-type LIB obtained by LDM for smart fabrics.[82] They used natural graphite and $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ as electrode materials. The 3D printed prototype displayed remarkable flexibility and chemical performance.

As a conclusion, several attempts to obtain flexible and wearable energy storage devices by LDM have been made but this is yet an immature technology and more investigation is needed before manufacturing LDM wearable batteries at a large scale.

2.1.2 | Fusion deposition modeling

FDM[95](Figure 5B) technology appears as an alternative to LDM. Researchers are looking for new polymer composites with enhanced properties suitable to feed FDM-printers because this method does not require post-processing and the fed polymer materials are cheap. Moreover, energy storage devices obtained by FDM[96] possess scalability, low-price, customizable properties and they can be obtained with environmentally friendly biopolymers.

For illustration, Maurel et al[83] described some filaments composed by poly lactic acid (PLA) and carbon black composite specifically conceived for LIB electrodes. The polymeric material was obtained by solution method, while a poly ethylene glycol was added to increase flexibility and abolish possible complications in the impression. When the solution was perfectly uniform, the excess of solvent was evaporated by the cast method. Once the film was cut, they obtained the filament by melt-extrusion. They also reported another PLA conductive filament for LIB obtaining[84] with a new method which did not need toxic solvents for its production because the filament was made directly in the extruder. Later, the same researchers detailed a new polymer composite with lithium charges (polyethylene glycol [PEO]/LiTFSI) suitable for LIB electrolyte material.[72] The process flowchart is like the first one hence, a complete LIB can be printed by FDM. The highest conductivity was obtained with a 20:1 PEO/LiTFSI ratio.

The previous polymeric LIB prototypes were all obtained by FDM however, their lack of flexibility disables them for wearable applications.

SC are mainly obtained by 3D printing and coating methods accordingly so, FDM processes are suitable.[74] For illustration, Ghosh et al[85] reported a filament polymeric composite suitable for LIB and SC electrodes composed by PLA, graphene, and metal-based impurities like iron and titanium oxides. Some commercial PLA/graphene filaments were modified with oxide impurities to enhance their electrochemical properties. The resultant material was tested in SC devices showing higher pseudocapacitance properties than the commercial one.

FDM is easily scalable, the prototyping is very quick and customizable to each concrete application. Moreover, some thermoplastics can be flexible, so this technology is presented as a good option for wearable energy storage devices. However, there is a lack of functional and suitable materials currently and therefore more investigation in the field is needed.

2.1.3 | Other AM techniques (SLA and digital light processing)

Other AM techniques which can be used in batteries manufacturing are SLA and digital light processing (DLP). Both capable of printing complex structures with high resolution using photocurable polymers.[97] As illustration, Arias-Ferreiro et al[86,98] reported a photocured polyaniline (PANI)/acrylate polymer composite obtaining suitable electrical and electrochemical properties for SC. Despite SLA and DLP technologies are able to print flexible and customized devices, they do not allow the integration of different components in the same process, so they are not the most suitable obtaining technique for energy storage devices in the present.

2.1.4 | Electrospinning

The electrospinning technique offers a high production rate, uniformity, high nanofiber quality, large surface areas, and low cost.[99,100] Nanofibers are better than other 1D nanomaterials (nanotubes, nanorods, nanowires, etc.) because once collected they do not need further purification, while they provide enhanced mechanical strength. Furthermore, several nanoarchitectures (core-shell, hollow, porous, tube, cross-linked) can be obtained thanks to their variants as melt

electrospinning, emulsion electrospinning, needle-less electrospinning, or coaxial electrospinning.[101]

Polymers reinforced with nanofibers show better mechanical performance than the matrix alone because of the nanofiber's structural parameters of size, aspect ratio, and alignment. Moreover, electrospun fibers obtained from conductive polymers possess a huge electrical conductivity range (10^{-11}-10^{5} S cm^{-1}) making them suitable for energy storage applications. Lee et al[71] reviewed polymer materials (polyvinyl acetate [PVA], PLA, Cellulose, PEO, etc.) reinforced with functionalized carbon nano-fillers (carbon nano tubes [CNT], graphene, QD) prepared by electrospinning technique. These materials present large surface areas and porosity but nowadays they do not possess scalability. In addition, Robert et al[102] reviewed last advances on electrospinning techniques for lithium, sodium, and potassium ion batteries electrodes. They affirmed that new and flexible materials are needed to make potassium and sodium batteries succeeded.

As electrospinning-obtained electrodes for energy storage device recent example, Zhou et al[87] reported a lignin-derived electrospun carbon material with enhanced charge transport characteristics valid for both SC and LIB electrodes. The fibrous composite showed remarkable flexibility and durability, desirable properties in wearable devices.

Several electrospun polymers (poly propylene, PVDF, poly acrylonitrile, etc.) have been used as binders. Recently, Barbosa et al recently reported[88] an environmentally friendly LIB separator based on poly(hydroxy butyrate-co-hydroxyvalerate) (PHBV) (a new renewable polyester) and cobalt ferrite (CFO). The biopolymer matrix provided flexibility and biodegradability while the CFO added dielectric performance. The PHBV looks very promising in energy storage devices due to its intrinsic physical properties but currently its higher cost than other biopolymers due to its obtaining method limits its applications.

Regarding to SC devices, Cárdenas-Martínez et al[89] mentioned some SC electrodes made of PEDOT:PSS. The electrospun nanofibers obtained from the polymer solution were immersed into ethylene glycol to increase their electrical conductivity. Once the nanofibers were enhanced, they were deposited by spin-coating into a poly ethylene terephthalate flexible substrate completing the electrode which was tested in an all-solid-state SC prototype.

The same year, Li et al[90] reported a binder-free flexible electrode for all-solid-state SC made with 2D graphene nano-sheets embedded in 1D hollow N-doped carbon nanofibers (HN-CNF/graphene nanosheets [GN]). GN improve the accessible specific surface area, increasing the charge storage capacity, and the capacitance of the final composite. The electrodes were obtained by coaxial-electrospinning and a thermal treatment giving rise to a shell-core structure. An all-solid-state SC was created to check the electrodes properties and an excellent capacity retention (90% after 2000 cycles) was showed.

Despite electrospun polymers advantages, the technique requires the use of solvents in the process, usually toxic or low environmentally friendly. Also, electrospinning has a lack of scalability nowadays.

Once the obtaining methods are reviewing, the next step should be revising the available polymer composites structures for LIB and SC, discussing which of them are suitable ones in wearable devices, paying special attention to the flexibility, and durability that each one can develop.

2.2 | Common polymer composites structures in wearable energy storage

2.2.1 | Fibers

Wearable electronic devices require wearability, durability, and comfort to the person who wears them[8] so, most wearable electronics are developed in fabrics with 1D fiber-shape. 1D fibers possess flexibility and tailorability, necessary properties in daily garments for standing the tensile efforts that they are submitted to. They have micro or nano-sized diameter, which is a very suitable characteristic in energy storage because their high aspect ratio increases their permittivity.

The first fiber-shaped energy storage device reported was a SC.[103] A SC is very easy to build fiber-shaped because the general obtaining method does not even require a strict fabrication process, it involves just adding two thin-film electrodes into the electrolyte. By contrast, a LIB needs fiber-electrodes, which is a hard task to achieve, and more complicated components in its fabrication like conductive additives, separators, binders and packaging materials. Nevertheless, current energy storage studies are focused on the search of new fiber materials for SC and LIB.[82,104]

Flexible energy storage devices can be fiber or cable shaped, as it is shown in Figure 6. On the one hand, nanofibers are usually made with carbonaceous electrodes as CNTs, electrospun carbon nanofibers or graphene.[109,110] Their obtaining is directly thanks to AM and electrospinning techniques. On the other hand, cable-type requires coating process for increasing the conductivity, which usually comes with a lack of durability and flexibility. The energy-storage fabrics are mainly

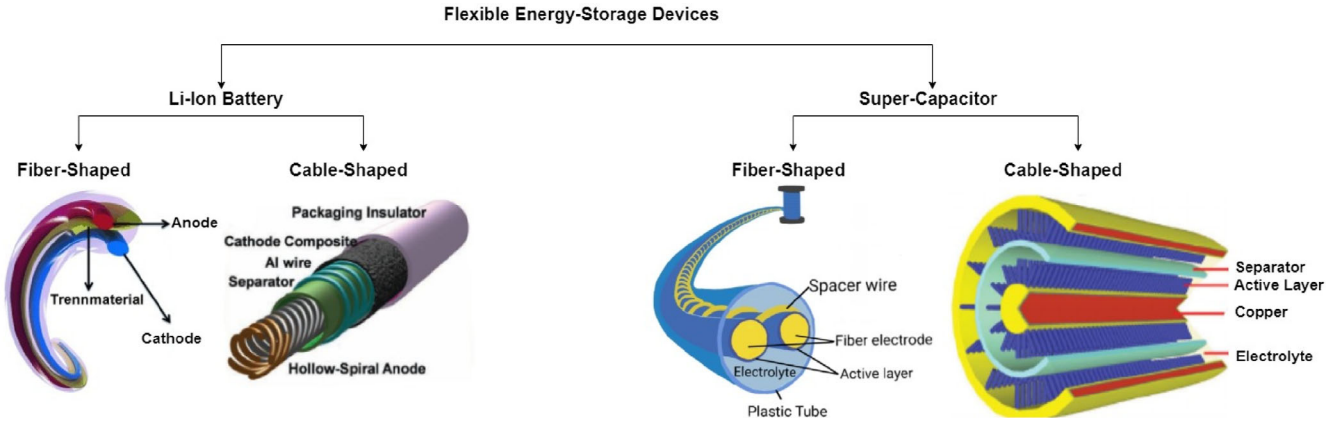


FIGURE 6 Main structures in wearable energy storage devices[105] redrawn,[106,107] redrawn.[108] Reproduced with permission. Copyright 2014, 2012, 2012, 2004, Wiley-VCH

obtained by coating deposition of yarn electrodes or polymeric fibers.[82]

As way of illustration, Lyu et al recently reported a grafted polymer network of carbon nanotube fibers to be used in fiber-shaped flexible SC.[104] They fabricated solid-state fibers (CNF/poly tri-phenyl amine [PTPA]) from PVA/H_3PO_4. The PTPA provides porosity and electrochemical activity while the CNF supplies high electrical conductivity, giving rise to a functional wearable energy storage device. Furthermore, Khudiyev et al[111] described a super-long SC fiber quite scalable to the industry, a 100 m long fully functional fiber which was tested in a 3D printing machine. The electrodes were made by thermally drawn gels with active material, carbon black, and PVDF (45:10:45). This study shows that supercapacitor fibers do not work only on a small scale but can be brought to industry.

The fabrication of fiber-shaped LIB carries on huge manufacturing problems, so they are conventionally fabricated in rigid structures, which are not suitable in wearable devices so, researchers should look for solutions and new materials. Recently, Lopez et al reported some LIB' anodes composed of TiO_2 and carbon. The composite was obtained by centrifugal spinning of precursor fibers (TiS_2/polyacylonitrile) and thermal post-processing. These new anodes developed better current densities in comparison with a graphite anode. Therefore, polymer materials could be useful in the progress of fiber-shaped LIB.

2.2.2 | Polymer meshes

Polymer meshes, composed by interconnected fibers assembled inside a polymer matrix, are also very present in wearable energy storage devices. Moreover, their planar-shape and their processing methods are accurate to LIB's obtaining. The polymer substrate (PVA, PA, PEO, poly vinyl pyrrolidone, PVDF, etc.) apports synthesis simplicity, flexibility, durability, and low cost while the filler (carbonaceous, mineral, etc) added by physical or chemical deposition, acts as the conductive component if necessary. The structure of these materials allows the obtaining of strength[112] fibrous mesh scaffolds, with appropriate characteristic for wearable electronic devices like high surface areas, remarkable ion conductivity, enhanced electrochemical response, adaptability, and stretchability.

Gong et al[21] reviewed the last progresses in polymer nanocomposites meshes. They classified them according to their obtaining method (natural meshes like cellulose fiber, electrospinning, in situ polymerization, and photolithography) and they concluded that electrospinning-based meshes were the most suitable for wearable devices.

Polymer nanocomposites meshes can be used in electrode materials or separators for energy storage devices, depending on their electrical conductivity response. As an example, Alameen et al[113] reported some flexible SC electrodes obtained by unipolar pulse electrodeposition of a C-ZIF-8/PANI composite film over the substrate. The electrodes were electrochemical tested in an acid solution and the enhancement in the cathodic peaks with the addition of the PANI was demonstrated. They also assembled a SC with PVA acting as electrolyte and separator and these new electrodes to probe its viability, getting remarkable power density.

Lately, Meng et al[114] also used PANI for SC electrodes but they electrodeposited the polymer on a Ti mesh substrate with MoO_3 particles. The final electrodes developed high capacity retention and capacitance under acid electrolyte, proving its viability as SC electrode.

TABLE 3 Energy storage performance and flexibility of different LIB and SC changing the structure of their materials

Material	Shape	Flexible	Capacitance ($F\ g^{-1}$)	Energy density ($W\ h\ kg^{-1}$)	Power density ($W\ kg^{-1}$)	Capacity retention	References
CNF/PTPA	Fiber SC	Yes	$*6.7 \times 10^{-2}$	$*1.83 \times 10^{-5}$	—	84% over 10 000 cycles	104
PVDF/CB	Fiber SC	Yes	4.34×10^{1}	—	—	100% over 13 000 cycles at 1.6 V	111
TiO_2/Carbon	Fiber LIB	Yes	6.18×10^{-3}	—	—	99.4% over 100 cycles	116
C-ZIF-8/PANI/SSWM	Mesh SC	Yes	3.63×10^{2}	9.16	162.5	100% over 10 000 cycles	113
PANI/Ti/MoO_3	Mesh SC	No	3.33×10^{3}	54	900	109% over 1000 cycles	114
$LiZnBO_3$/C	Mesh LIB	No	2.25×10^{-4}	334.8	—	94.47% over 600 cycles	115

Note: The values with * are $F\ cm^{-1}$ or $W\ h\ cm^{-1}$.
Abbreviations: CB, carbon black; CNF, carbon nano fibers; LIB, lithium-ion batteries; SC, super-capacitors; PANI, polyaniline; PTPA, poly tri-phenyl amine; PVDF, poly vinylidene fluoride.

Despite the viability of these materials in wearable energy storage devices, they are not all-polymeric, this is an important point because it hinders its disposal process once the life-time of the device ends. Moreover, inorganic conductive or semiconductive materials are not flexible and their elasticity is limited. Therefore, investigation should be focused on all-polymeric materials.

In addition, the investigation in polymer meshes materials for LIB is scarce. In 2016, Li et al reported some anodes for LIB based on $LiZnBO_3$ and carbon mesh synthesized by pyrolysis method.[115] The anode was tested with a commercial $LiCoO_2$ cathode obtaining remarkable energy density.

By last, the Table 3 collects the principal energy storage characteristics of the previous examples.

2.3 | Last developments in polymer composites for energy storage devices and their viability in wearable gadgets

Several polymer composites are promising materials in energy storage devices due to their low electric losses, high charge discharge speed, and high-power density. The polymer matrix adds processability, getting lightweight final components, and conductive nano-fillers provide electrical conductivity and sometimes mechanical reinforcement.[22] Table 4 summarizes the most used polymer matrixes in wearable batteries, it is divided in intrinsically conductive polymers, which are conductors themselves, and dielectrics, which are not.

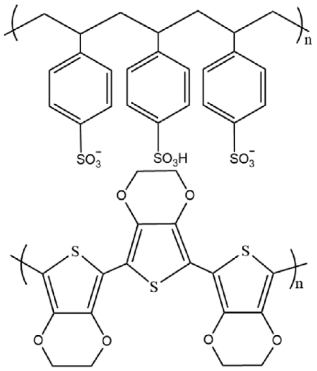
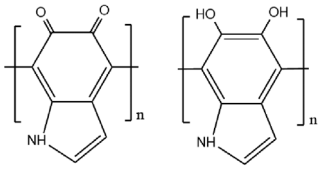
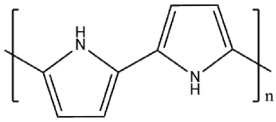
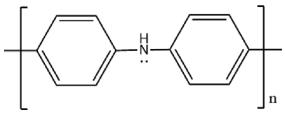
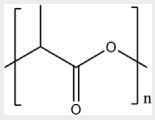
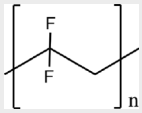
In some cases, the polymer composite contains an inorganic nano-filler (SiO_2, AlO_3, MgO, etc) inside a polymer matrix. The inorganic filler increases the polymer dielectric properties but, they are not the most environmental-friendly option so, all-polymeric (polymeric composites with organic fillers) electrodes and electrolytes are emerging due to the advantages that they provide.[121,122]

All-polymeric composites have good cycling stability, high power densities, and their capacitance increases due to the higher porosity of the conductive polymers.[50] They usually develop a high flexibility, but it comes at the expense of the electrical conductivity so, the optimal point between enhanced mechanical and electrical properties should be found.

Focusing on wearable energy storage devices fiber-like, 3D porous, and paper-like active materials are being studied for SC and LIB electrodes.[36] The fiber ones are the easiest to wove into clothes and they show enhanced physical properties (tensile strength and elastic modulus)[11] so, they are very present in wearable batteries. Regarding to the obtaining method, both 3D printers and electrospinning technique are capable of producing the fibers which give rise to the smart garments.

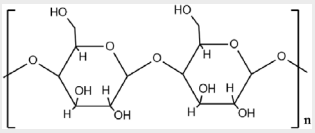
Next, the main characteristics of each polymer matrix are going to be explain adding studies as examples. The Table 5 collects the principal electrochemical parameters of these studies in order to compare their efficiencies.

TABLE 4 Common polymer matrixes in energy storage devices

Polymer	Electrical conductivity (S cm^{-1})	Advantages	Disadvantages	Molecular structures	References
ICP					
PEDOT:PSS	4.7×10^4	-High electrical conductivity -Commercially available as a water dispersion, lightweight	-Water dispersion possess much lower electrical conductivity (1 S cm^{-1}) thereby they need additives -Mechanical properties and processability of pure PEDOT:PSS need improvements		3
PDA	2.6×10^5	-Easy synthesis by exposing dopamine to air -Good as coated material, it adds resistance -Easily functionalization	-Difficult control of the material architecture -Its structure is not completely studied yet		117
PPY	10-50	-Low cost, easy preparation and modification -It is soluble in water -There is a lot of information about how to work with this material	-Poor mechanical properties such as brittleness -Poor thermal stability in air -It is a non-biodegradable material		118
PANI	7.25	-Easy doped/undoped material thanks to the -NH group -Good electrochemical and thermal stability	-Poor electrical conductivity		86
Dielectric					
PLA	—	-Cheap -Mechanical strength -Biopolymer and biodegradable -It only requires little energy on its production	-Low glass transition temperature (about 55°C), which make it unsuitable in applications that require more thermal stability -Poor ductility		62
PVDF	10^{-5}	-Thermodynamically stable in its β phase -Piezoelectric polymer	-Low energy conversion efficiency -Low output power -Poor mechanical strength -Elevated cost		119

(Continues)

TABLE 4 (Continued)

Polymer	Electrical conductivity (S cm^{-1})	Advantages	Disadvantages	Molecular structures	References
Cellulose	—	-Biopolymer abundant in nature -Nontoxic, biodegradable, and renewable material -Widely studied	-Poor resistance to water -It requires long time to compost		23,120

Abbreviations: ICP, intrinsically conducting polymers; PANI, polyaniline; PDA, polydopamine; PLA, poly lactic acid; PPY, polypyrrole; PVDF, poly vinylidene fluoride.

2.3.1 | Polymer composites with ICP matrixes

Conductive polymers are wide used in both SC and LIB electrodes due to its unique electronic properties, their large surface areas, and their remarkable electrochemical properties.[74,118]

PEDOT:PSS

The most widely studied ICP is PEDOT:PSS due to its stability, high conductivity, and water resistance, making them suitable for roll-to-roll manufacturing. Tseghai et al[3] reviewed the PEDOT:PSS conductive textiles and their obtaining methods. PEDOT:PSS can be deposited on a textile flexible substrate by an in-situ polymerization, by fiber spinning process or by printing textile fabrics. The authors conclude that the processes obtain conductive fabrics with enhanced flexibility and mechanical resistance, but their electrical conductivity decreases during the process.

Mostly, PEDOT:PSS composites for wearable energy storage devices are found with fiber-shape[123-125] because of their lightweight and mechanical flexibility. And as it was discussed before, fiber-shaped energy storage devices are mainly SC.

Recently, Mirabedini et al[123] described a PEDOT:PSS-based polymer composite for SC electrodes. The CNT fibers were coated to the PEDOT:PSS matrix by coaxial wet-spinning method, adding flexibility to the composite and its enhanced mechanical properties. The SC possess a thickness lower than 100 μm, which brings low weight to the device, and it is highly flexible, both properties are desirable for wearable devices. In addition, the gadget is able to perform a remarkable power density.

Liu et al[124] also mentioned some PEDOT:PSS fibers for wearable SC applications but with rGO instead of CNT as electrical conductive nanofiller. The fibers were obtained in a tube mold by hydrothermal confinement process, a very easy processing method which enhanced the capacitive properties of the material thanks to the cross-linking between the rGO and the polymer matrix. The final prototype possesses remarkable flexibility and tensile strength.

Moreover, Teng et al[125] reported a similar PEDOT:PSS/rGO fiber SC which were also obtained by a confined growth process but they tried post processing with anacid treatment. This new procedure got enhanced electrical conductivity and partial capacitance thanks to the fast ions diffusion throughout the porous channels of the nanofiller inside the PEDOT:PSS matrix. In summary, they obtained a SC with high capacitance and astounding capacitance retention.

The wearable SC devices are not only presented as fiber-shaped but also as paper and film. To way of illustration, Song et al[126] demonstrated some paper-shaped flexible SC composed by PEDOT:PSS as polymer matrix, which provides toughness, flexibility, and structural stability, rGO, and CNT as electrically conductive nanofillers and Fe_2O_3 to increase the electrochemical performance of the new composite. The final electrode demonstrated high specific capacitance.

In addition, Huang et al[127] recently reported a PEDOT:PSS/carbon nanocoils polymer composite to obtain SC electrodes with film-shaped. The polymer matrix apported mechanical stability while the nanofillers allows the formation of interconnected hierarchical pores, which operate as ions transport channels, shortening the diffusion pathways, and as electrolyte storage reservoir. This composite was obtained by repeated drop-casting technique, which facilitates its processability. The final film-shaped electrode developed notable electrochemical properties as well as enhanced flexibility (twisting and bending resistance).

The previous studies seem a good advance to get wearable SC but their obtaining methods are testing only at laboratory scale. In conclusion, it is necessary to get materials not only with high electrochemical performance, enhanced flexibility, and mechanical resistance but also scalable to industrial manufacturing.

TABLE 5 All-polymeric energy storage devices with different matrixes

Matrix	Filler	Additives	Obtaining method	Capacitance ($F\ g^{-1}$)	Energy density ($W\ h\ kg^{-1}$)	Power density ($W\ kg^{-1}$)	Capacity retention	Applications	References
Intrinsically conducting polymer matrixes									
PEDOT:PSS	CNT fiber	MnO_2	Wet-spinning	1.51×10^{-2}	5.83	1399	84% over 1000 cycles	All-in-one fiber flexible SC	123
PEDOT:PSS	rGO	—	Hydrothermal confinement reaction	2.5×10^{2}	10.68	81.25		Paper electrodes for flexible SC	124
PEDOT:PSS	rGO	—	Confined growth+ acid treatment	$*2.27 \times 10^{2}$	$*5.6 \times 10^{-3}$	$*1.98 \times 10^{-5}$	91% over 10 000 cycles	Fiber shaped flexible SC	125
PEDOT:PSS	rGO/CNT	Fe_2O_3	Vacuum drying	$*1.92 \times 10^{-6}$	35.6	166	98.2% over 10 000 cycles	Paper-shaped electrodes for flexible SC	126
PEDOT:PSS	Carbon nanocoils	—	Drop-casting	—	5.16	172.4	—	Film-shaped electrodes for flexible SC	127
PEDOT	Silicon	—	Wet chemical process	4.36×10^{-2}	—	—	—	LIB electrodes	128
PDA	NiS	NC	Polymerization and pyrolysis	1.33×10^{3}	28.6	884.5	81.7% over 3000 cycles	SC electrodes	129
PDA	rGO	Co_3O_4	In situ growth	1.56×10^{3}	46.1	800	91% over 10 000 cycles	SC electrodes	130
PDA	CNF	$Zn(CF_3SO_3)_2$	Dip coating	1.39×10^{-2}	≈260	≈520	80% over 1700 cycles	Organic cathode in wearable zinc batteries	131
PPY	Carbon cloth	HCl	Electrochemical deposition	9.6×10^{2}	6.2	2.64×10^{3}	88% over 6000 cycles	Flexible SC electrodes	132
PPY	Carbon thread	Cellulose acetate fibers	Functionalization	2.3	3.9×10^{-1}	46 400	100% over 1000 cycles	Yarn-based flexible SC	133
PPY	CNT	—	In situ polymerization	$\wedge 3.87 \times 10^{-1}$	1.32×10^{-5}	2.78×10^{-4}	87.8% over 5000 cycles	Flexible SC	134
PPY	Graphite	$ZnMn_2O_4$	Polymerization	4.61×10^{-3}	64	11.7×10^{3}	80.3% over 1000 cycles	Flexible Zn batteries cathodes	135
PANI	PVA	—	Supramolecular strategy	$\wedge 1.52 \times 10^{-1}$	—	—	79.5% over 5000 cycles	Wearable electrodes for SC and LIB	136
PANI	GO, CNT	MnO_2, ZnO	Interfacial polymerization	7.29×10^{2}	11.7	250	80% over 500 cycles	Solid state SC electrodes	137
PANI	rGO	Au, φMnO_2	Electrochemical synthesis	5.57×10^{2}	—	—	70% over 2000 cycles	Film-shaped SC electrodes	138
PANI	PVA	H_3PO_4	Electrodeposition route	2.82×10^{2}	—	—	55% over 200 cycles	Flexible SC electrodes	139
Dielectric polymer matrixes									
PLA	Graphene, MWCNT	LTO, $LiMn_2O_4$	Solvent casting+ filament extrusion	$* \approx 10^{-4}$	—	—	100% over 100 cycles	3D printed LIB	140
PLA	PPY/GO	$FeCl_3$	Coated+ polymerization	$\wedge 1.59 \times 10^{-1}$	$\wedge 3.5 \times 10^{-6}$	$\wedge 3.2 \times 10^{-5}$	—	Flexible SC electrodes	141
PLA	Graphite	PEG	Film-casting	$\wedge 1.9 \times 10^{-3}$	—	—	100% over 5000 cycles	Flexible SC electrodes	142

(Continues)

TABLE 5 (Continued)

Matrix	Filler	Additives	Obtaining method	Capacitance ($F g^{-1}$)	Energy density ($W h kg^{-1}$)	Power density ($W kg^{-1}$)	Capacity retention	Applications	References
PVDF-HFP	SWCNT	MnO_2	Drop casting	1.1×10^2	23	$11 \cdot 10^3$	—	Flexible SC electrodes	143
PVDF-HFP	CNT	LTP/LVP	Drop-coating	4.99×10^{-3}	—	—	75% over 2000 cycles	Electrolyte for all-solid state flexible LIB	59
Cellulose	rGO	PDA	In-situ polymerization + functionalization	^3.1	—	—	94% over 7000 cycles	Flexible SC electrode	144
Methyl cellulose	CoFe2O4	—	Chemical deposition	4.33×10^2	73	1.1×10^3	89% over 2000 cycles	Flexible SC cathode	145

Note: The values with ^ are F cm^{-2}, W h cm^{-2} or W cm^{-2} and the values with * are F cm^{-3}, W h cm^{-3} or W cm^{-3}).
Abbreviations: CNT, carbon nano tubes; GO, graphene oxide; MWCNT, multi-walled carbon nanotubes; PANI, polyaniline; PDA, polydopamine; PPY, polypyrrole; PVA, polyvinyl acetate; PVDF, poly vinylidene fluoride; rGO, reduced graphene oxide; SC, super-capacitors.

Despite PEDOT:PSS conductive composites are mainly used in SC some authors propose to use them in LIB components, as polymer binders[146,147] or anodes.[128] However, these studies developed rigid prototypes, which are not useful in wearable LIB.

PDA

Another important ICP is the PDA,[148] which is obtained by the oxidation of dopamine, a quinone material. PDA is composed by an isomeric mixture of tetramers and octamers induced by a constant redistribution of the electrons from the ketone groups resulting in enhanced specific capacitance. In addition, PDA is a biopolymer which gives rise to environmental friendly energy storage devices with a fast and reversible redox activity, developing a remarkable electrochemical performance[149,150] so it is very useful for the obtaining of SC electrodes. As way of illustration, Zhu et al reported some PDA-based polymer electrodes for supercapacitors[129] with NiS particles acting as filler. They obtained the new polymer composite by PDA polymerization on the NiS surface, getting an interconnected network framework and superior N doping, and posterior pyrolysis, improving the specific capacity of the electrodes. The composite was synthesized with a core-shell structure, developing an enhanced electrochemical performance because it helped with the adaptation of the material to the volumetric changes during the charge/discharge processes.

Moreover, Tian et al mentioned[130] some SC electrodes formed with PDA matrix, rGO as organic conductive nanofiller and Co_3O_4 nanorods as inorganic filler. The Co_3O_4 helps with the charge storage, but it usually suffers deactivation during de charge/discharge process. However, this PDA/rGOCo_3O_4 composite keeps the nanorods activated thanks to the reversible redox reaction that the PDA/rGO composite apports to the electrode. This novel composite develops electrodes for cycle stable, durable, and robust SC.

Both studies[129,130] show great promise for obtaining electrodes for SC based on materials from nature, however, they are rigid materials so they cannot be used in wearable energy storage devices.

The PDA can develop flexible devices[151] if the correct fillers are selected. Recently, Wang et al[131] reported a PDA-based material for aqueous zinc batteries. They used some CNF as organic substrate and coated them with PDA, obtaining organic cathodes. The final power fibers possess high capacity, energy density, flexibility, and strength resistance. The organic fibers are washable and they can be processed by a sewing machine, so its implementation in the fabrics is direct. So, this new technology looks very promising in the next generation of wearable energy storage devices.

PPY

PPY is another ICP suitable for energy storage devices. This polymer develops superior environmental stability and biocompatibility, making itself very useful in a wide range of applications and it possess intrinsic flexibility, desirable property in wearable devices. It can be synthesized using electrochemical or chemical polymerization techniques and its conductivity comes from a p-type doping.[118]

Several authors propose to use PPY in the design of new SC.[132-134] For illustration, Zhang et al[132] recently reported SC electrodes composed by carbon cloth coated with PPY films electrochemically deposited. They used HCl as acid dopant in the PPY films to make them more flexible achieving an enhanced specific capacitance. The assembled flexible SC is suitable for wearable energy storage applications however, its cycling stability is quite poor, so its durability is compromised.

In addition, Lima et al[133] described very novel a symmetrical wire-shape SC composed by functionalized carbon threads with PPY as electrodes. The resulting SC is the first to use the wearer's sweat as an electrolyte, and it demonstrated a very high power density. Moreover, the prototype is flexible and possess remarkable stability under mechanical deformation. However, it possesses very low energy density, which can be a problem for some concrete applications.

Later, Hao et al[134] mentioned a twisted yarn-shaped SC composed by PPY/CNT electrodes. They were acquired by in situ polymerization of PPY on CNT and posterior inlay of it into cotton yarns. PPY/CNT electrodes demonstrated remarkable electrical conductivity ($20\ \Omega\ cm^{-1}$), cycle stability, and capacitive performance. The SC prototype exhibited lightweight, small volume, and high energy density, providing a wearable yarn-shaped SC.

Regarding the next-generation energy storage devices, Li et al[135] recently fabricated a Zn battery cathode composed by graphite nano-platelets (short stacks of platelet-shaped graphene sheets) coated with PPY via in situ polymerization. The prototype showed remarkable porosity and a super high power density.

To achieve commercial wearable energy storage devices with PPY-based flexible composites it is necessary to advance in industrially scalable processing techniques.

PANI

The PANI is an ICP used in SC and LIB.[152] This polymer is very easy to dope so both the electronic conductivity and the color can be modified making PANI a suitable material for electronic devices. Due to its high specific capacitance ($2 \times 10^3\ F\ g^{-1}$) it is used for increasing the specific capacitance of other polymers for energy storage devices.

For instance, Chu et al[136] described some ultrathin electrode for all-solid state wearable energy storage devices composed of PANI and PVA membranes. The PANI/PVA was obtained by crosslinking reaction between PANI chains and PVA creating a robust, flexible, foldable, and freestanding membrane.

Regarding SC electrodes, Jiang et al recently[137] reported an all-organic PANI/GO/CNT composite suitable for wearable SC electrodes. They obtained the composite in different forms (helical fibers and planar films) to obtain a higher adaptability to multiple applications, and both showed excellent electrochemical behavior. The combination of the PANI with the conductive nanofillers develops electrodes with remarkable electrochemical performance, flexibility and stability under deformation conditions, required properties in wearable energy storage devices.

Taravati et al also mentioned[138] some electrodes for SC based on PANI but with inorganic filler. They synthesized by electrochemistry φMnO_2 and Au particles on stainless steel mesh which was coated with GO immediately after. Then, the PANI was added by in situ polymerization reaction, obtaining some polymer nanocomposite films. The electrodes developed superior reversible capacitance and remarkable recyclability.

In addition, Huang et al described[139] other SC using PANI electrodes and a high strain resistant hydrogel (PVA/H_3PO_4) electrolyte. The novel SC was obtained by electrodeposition route, a cost-effective and facile technique. The device showed enhanced stretchability and flexibility due to the intrinsic properties of the polymeric electrodes and electrolyte. This approach of getting polymeric SC gets organic devices with superior recyclability, mechanical resistance, flexibility, and adaptability.

As a conclusion, all this studies about PANI uses in wearable energy storage devices is going to be very useful for the upcoming devices do to the polymer' intrinsic properties.

2.3.2 | Polymer composites with dielectric polymers matrixes

Dielectric polymer materials possess remarkable properties such as low electric losses, high flexibility, high electric breakdown field and an easy preparation. That is why they are suitable in wearable energy storage devices.

PLA

PLA, a bio-based and compostable amorphous thermoplastic polyester, is the most used fed material in 3D printers because it is easily printable and it possess interesting mechanical properties. It is obtained from natural

resources as sugar cane, corn starch, or potato so it is biodegradable under certain conditions. The PLA can be easily processed by multiple standard techniques such as FDM, injection molding, or extrusion. Some authors propose to fabricate a conductive filament by extrusion based on PLA for the obtaining of flexible energy storage devices by FDM 3D printing.[153] Currently, there is a commercial PLA is conductive nanofiller called Blackmagic which is very useful for the study and obtaining of 3D printed electrodes.[154,155] This method possesses several advantages as rapid design, low-cost materials, repeatability, customizability, and the most important: scalability. Following this strategy, Reyes et al reported[140] a LIB prototype all 3D printed with PLA, different conductive nanofillers (graphene, MWCNT and more), and several active materials (LTO and $LiMn_2O_4$). They demonstrated the possibility of creating wearable devices printing a bracelet and some glasses.

As it was discussed before, despite the advantages 3D printed energy storage devices obtained from conducting PLA composites, currently the maximum of the material properties has not been obtained yet. As a conclusion, novel and enhanced PLA polymer composite materials are needed to boost the next-generation of wearable batteries.

From a different approach, Nie et al[141] recently reported a fiber-shaped SC based on PLA filament coated GO/PPY polymer hybrid acting as conductive filler. The PLA matrix allows the addition of high loading of the active material while it contributes to the stability of the composite. The final electrodes developed flexibility, enhanced energy density, and capacitance even under bending deformation.

Recently, Jellet et al[142] mentioned some PLA/graphite flexible electrodes with film shape. The polymer composite developed superior electrical conductivity owing to its high nanofiller content (around 64 wt%) and enhanced flexibility thanks to the PLA matrix and the film shape. In addition, its electrochemical performance did not decrease when it was working under bending forces, making it valid for wearable energy storage devices.

PVDF

Another dielectric material used in **polymer** composites preparation is the PVDF, a semi-crystalline polymer with enhanced properties in energy storage.[111] This polymer possesses remarkable dielectric properties in virtue of its ferroelectric phase and superior mechanical resistance.[69]

As way of illustration, He et al[143] mentioned a flexible and wearable SC device composed by PVDF-HFP/single walled carbon nano tubes electrodes sandwiched between self-healing layers, providing durability and flexibility to the device. The electrodes were obtained in film shape by drop-casting method with superior thickness (80 μm). Then, the anode, cathode, and electrolyte were assembled by hot-pressing molding. After, the novel SC preparation it was integrated for the first time with a mechanical energy harvester device getting an auto-fed wearable electronic device. This study offers up possibilities for the flexible and wearable technology to be further developed for future energy storage and harvesting applications.

In addition, Yu et al[59] described a nontoxic and safe wearable energy storage device composed by PVDF-HFP as electrolyte material and CNT as conductive electrodes. They obtained the CNT electrodes from the calcination of a CNT fabric, later the PVDF-HFP electrolyte was added by drop-coating and tape casting to fill both the pores and the surface of the electrodes. Finally, a flexible all-solid-state LIB with enhanced electrochemical properties was obtained.

Cellulose

One renewable alternative to these materials and abundant in nature is the cellulose biopolymer, the most abundant biopolymer on earth.[156] It is formed by carbon, hydrogen, and oxygen molecules making a complex polysaccharide. Cellulose presents a wide electrochemical stability window, superior physical properties, and enhanced thermal stability thereby some authors consider it as a good candidate to use as SC electrodes.[23,120]

Recently, Chen et al[144] propose to use the cellulose as flexible substrate for a cellulose/rGO/PDA polymer composites. This material serves as conductive and active material, and as a binder owing to move between the N-doped carbon interface and the adhesive PDA interface. The obtained electrodes developed high specific area, porosity, enhanced charge transport, and remarkable capacitance suitable for wearable all-solid-state SC.

Later, Haghshenas et al[145] reported another new nanocomposite base on cellulose compose by methyl cellulose and $CoFe_2O_4$. The material was obtained by chemical deposition method and by hydrothermal method but only the first one succeeded. The nanocomposite was disposed as cathode in an asymmetric SC, obtaining high capacity retention and cycling stability.

These new polymer composites, based in a biopolymer matrix, abundant in nature and biodegradable are displayed as possible materials for next-generation wearable storage devices thanks to their flexibility, adaptability, long-life, and remarkable electrochemical properties.

3 | CONCLUSION, FUTURE CHALLENGES, AND INVESTIGATION PERSPECTIVES

Nowadays, researchers are looking for enhanced batteries, with improved properties thereby, new materials are

being investigated to overcome the actual challenges. These new materials should be flexible, lightweight, and tailorable to fit in the wearable devices. They also have to present better electrical performance to improve the energy storage properties.

The first aim should be the obtaining of new longer-life materials to tackle actual demands from electronic devices, cars, wearable devices, and more technology. These new longer-life materials will be able to sustain a higher number of charge/ discharge cycles giving rise to better batteries.

The investigation should focus on nontoxic, environmental-friendly and even recyclable or biodegradable materials. Polymer composites are a suitable option for new components of batteries because they can possess all the aforementioned requirements.

The third improvement topic is the electrical characteristics of current store devices: energy and power densities. SC show low energy densities and LIB low power densities therefore the new material developments should overcome these shortcomings. Both parameters are affected with the election of the active materials. New active materials are appearing as graphite substitute (in LIB) with better current capacities. These new materials are dealing with a lack of adaptability at the volumetric changes that they suffer on the charge/discharge processes.

In addition, mechanical properties suitable for a specific application should be developed to keep the battery performance during its service life. Some authors propose to improve it with reinforced materials, adding some mechanical resistant one. In this field, the waste recovery is gaining a lot of importance because some materials such as the lignin, a natural polymer, that can be used as mechanical reinforcement in polymer composites.

Focusing on the material sustainability it is not only necessary to use bio-based materials, like biopolymers, but also obtain the different batteries components by eco-friendly processes. Nowadays, the carbon footprint of each single process should be taking on account. Furthermore, once the battery is not more useful all their parts should have an easy recycling process so they will not be a waste problem.

By last, the new materials should reach the industry level so more effort should be focused on industrial scale-up of those materials that have demonstrated better properties at laboratory scale.

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

ORCID

Silvia Lage-Rivera https://orcid.org/0000-0003-3889-3847

REFERENCES

1. Mokhtari F, Spinks GM, Fay C, et al. Wearable electronic textiles from nanostructured piezoelectric fibers. *Adv Mater Technol*. 2020;5:1.
2. Xie J, Wang Y, Dong R, Tao K. Wearable device oriented flexible and stretchable energy harvester based on embedded liquid-metal electrodes and FEP electret film. *Sensors*. 2020;20:458.
3. Tseghai GB, Mengistie DA, Malengier B, Fante KA, Van Langenhove L. PEDOT: PSS-based conductive textiles and their applications. *Sensors*. 2020;20:1.
4. Mokhtari F, Cheng Z, Raad R, Xi J, Foroughi J. Piezofibers to smart textiles: a review on recent advances and future outlook for wearable technology. *J Mater Chem A*. 2020;8:9496-9522.
5. Nguyen DN, Moon W. Photocurable bulk epoxy resins based on resorcinol derivative through cationic polymerization. *J Appl Polym Sci*. 2020;137:49051.
6. Tajitsu Y. Development of e-textile sewn together with embroidered fabric having motion-sensing function using piezoelectric braided cord for embroidery. *IEEE Trans Dielectr Electr Insul*. 2020;27:1644-1649.
7. Li X, Chen S, Zhang X, et al. Poly-L-lactic acid/graphene electrospun composite nanofibers for wearable sensors. *Energy Technol*. 2020;8:1.
8. Kim J, Byun S, Lee S, et al. Cost-effective and strongly integrated fabric-based wearable piezoelectric energy harvester. *Nano Energy*. 2020;75:104992.
9. Satharasinghe A, Hughes-Riley T, Dias T. An investigation of a wash-durable solar energy harvesting textile. *Prog Photovolt Res Appl*. 2020;28:578-592.
10. Sunitha AP, Sandeep K, Praveen P, Saji K. Upconverting carbon quantum dots: an eco-friendly material for light energy harvesting and bio-imaging. *J Mater Today Proc*. 2020;33:1298-1300.
11. Burela RG, Kamineni JN, Harursampath D. *3D and 4D Printing of Polymer Nanocomposite Materials*. Amsterdam, Netherlands: Elsevier; 2020. https://doi.org/10.1016/B978-0-12-816805-9.00008-9
12. Yi FL, Meng FC, Li YQ, et al. Highly stretchable CNT fiber/PAAm hydrogel composite simultaneously serving as strain sensor and supercapacitor. *Compos Part B Eng*. 2020;198:108246.
13. Bagarti T, Jayannavar AM. Storage of electrical energy: batteries and supercapacitors. *Resonance*. 2019;25:963-980.
14. Olabi AG, Sayed ET, Wilberforce T, et al. Metal-Air Batteries—A Review. *Energies*. 2021;14:7373.
15. Fu J, Cano ZP, Park MG, Yu A, Fowler M, Chen Z. Electrically rechargeable zinc-air batteries: progress, challenges, and perspectives. *Adv Mater*. 2017;29:1604685.
16. Cao D, Shen X, Wang Y, et al. Conductive polymer coated cathodes in Li–O_2 batteries. *ACS Appl Energy Mater*. 2020;3:951-956.

17. Zhang C, Huang K. A Comprehensive Review on the Development of Solid-State Metal–Air Batteries Operated on Oxide-Ion Chemistry. *Adv Energy Mater*. 2021;11:1.
18. Chen X, Ali I, Song L, et al. A review on recent advancement of nano-structured-fiber-based metal-air batteries and future perspective. *Renew Sustain Energy Rev*. 2020;134:110085.
19. Li Y, Lu J. Metal–air batteries: will they be the future electrochemical energy storage device of choice? *ACS Energy Lett*. 2017;2:1370-1377.
20. Wang C, Yu Y, Niu J, et al. Recent progress of metal–air batteries—a mini review. *Appl Sci*. 2019;9:1.
21. Gong M, Zhang L, Wan P. Polymer nanocomposite meshes for flexible electronic devices. *Prog Polym Sci*. 2020;107:101279.
22. Gong X, Yang Q, Zhi C, Lee PS. Stretchable energy storage devices: from materials and structural design to device assembly. *Adv Energy Mater*. 2021;107:2003308.
23. Anthony LS, Vasudevan M, Perumal V, Ovinis M, Raja PB, Edison TNJI. Bioresource-derived polymer composites for energy storage applications: brief review. *J Environ Chem Eng*. 2021;9:105832.
24. Lizundia E, Kundu D. Advances in natural biopolymer-based electrolytes and separators for battery applications. *Adv Funct Mater*. 2020;31:2005646.
25. Liu C, Yan X, Hu F, Gao G, Wu G, Yang X. Toward superior capacitive energy storage: recent advances in pore engineering for dense electrodes. *Adv Mater*. 2018;30:1705713.
26. Gopi CV, Vinodh R, Sambasivam S, Obaidat IM, Kim HJ. Recent progress of advanced energy storage materials for flexible and wearable supercapacitor: from design and development to applications. *J Energy Storage*. 2020;27:101035.
27. Miller EE, Hua Y, Tezel FHJ. Materials for energy storage: review of electrode materials and methods of increasing capacitance for supercapacitors. *Energy Storage*. 2018;20:30-40.
28. Zhang D, Tan C, Zhang W, Pan W, Wang Q, Li L. Expanded graphite-based materials for supercapacitors: a review. *Molecules*. 2022;27:716.
29. Wang H, Niu H, Wang H, et al. Micro-meso porous structured carbon nanofibers with ultra-high surface area and large supercapacitor electrode capacitance. *J Power Sources*. 2021;482:228986.
30. Hu H, Zhang F, Luo S, Chang W, Yue J, Wang C-H. Recent advances in rational design of polymer nanocomposite dielectrics for energy storage. *Nano Energy*. 2020;74:104844.
31. Maletin YA, Stryzhakova NG, Zelinskyi SO, Chernukhin SI. Energy storage technologies based on electrochemical double layer capacitors: a review. *Theor Exp Chem*. 2022;57:267-324.
32. Liu K, Yu C, Guo W, et al. Recent research advances of self-discharge in supercapacitors: mechanisms and suppressing strategies. *J Energy Chem*. 2021;58:94-109.
33. Fleischmann S, Mitchell JB, Wang R, et al. Pseudocapacitance: from fundamental understanding to high power energy storage materials. *Chem Rev*. 2020;120:6738-6782.
34. Choudhary RB, Ansari S, Majumder M. Recent advances on redox active composites of metal-organic framework and conducting polymers as pseudocapacitor electrode material. *Renew Sustain Energy Rev*. 2021;145:110854.
35. Shen X, Li Z, Deng N, et al. Rational designing of tree-like polymer gel membrane based on PVDF/lamellar organic montmorillonite nanofiber with excellent flame retardancy and superior ion conductivity for high-performance lithium-ion capacitor. *Chem Eng J*. 2021;422:130116.
36. Raza W, Ali F, Raza N, et al. Recent advancements in supercapacitor technology. *Nano Energy*. 2018;52:441-473.
37. Zhao J, Burke AF. Electrochemical capacitors: materials, technologies and performance. *Energy Storage Mater*. 2021;36:31-55.
38. Rani JR, Thangavel R, Oh SI, Lee YS, Jang JH. An ultra-high-energy density supercapacitor; fabrication based on thiol-functionalized graphene oxide scrolls. *Nanomaterials*. 2019;9:1.
39. Sagaria S, Costa Neto R, Baptista P. Assessing the performance of vehicles powered by battery, fuel cell and ultracapacitor: application to light-duty vehicles and buses. *Energy Convers Manage*. 2021;229:113767.
40. Chen F, Liu C, Cui B, et al. Regulated synthesis of Eutectic Ni3S2/NiS nanorods for quasi-solid-state hybrid supercapacitors with high energy density. *J Power Sources*. 2021;482:228910.
41. Sha Z, Huang F, Zhou Y, et al. Synergies of vertical graphene and manganese dioxide in enhancing the energy density of carbon fibre-based structural supercapacitors. *Compos Sci Technol*. 2021;201:108568.
42. Zhou Y, Obeid H, Laghrouche S, Hilairet M, Djerdir A. A novel second-order sliding mode control of hybrid fuel cell/super capacitors power system considering the degradation of the fuel cell. *Energy Convers Manage*. 2021;229:113766.
43. Singh A, Karandikar PB, Kulkarni NRJ. Mitigation of sulfation in lead acid battery towards life time extension using ultra capacitor in hybrid electric vehicle. *Energy Storage*. 2021;34:102219.
44. Zhang G, Li Q, Chen W, Meng X. Synthetic strategy combining speed self-adjusting operation control and adaptive power allocation for fuel cell hybrid tramway. *IEEE Trans Ind Electron*. 2021;68:1454-1465.
45. Veerendra AS, Mohamed MR, Leung PK, Shah AA. Hybrid power management for fuel cell/supercapacitor series hybrid electric vehicle. *Int J Green Energy*. 2021;18:128-143.
46. Atta MM, Fahim RAJ. Flexible and wearable supercapacitors: a short review. *Energy Storage*. 2021;44:103475.
47. Raj CJ, Manikandan R, Cho WJ, Yu KH, Kim BC. High-performance flexible and wearable planar supercapacitor of manganese dioxide nanoflowers on carbon fiber cloth. *Ceram Int*. 2020;46:21736-21743.
48. Aldalbahi A, Samuel E, Alotaibi BS, El-Hamshary H, Yoon SS. Reduced graphene oxide supersonically sprayed on wearable fabric and decorated with iron oxide for supercapacitor applications. *J Mater Sci Technol*. 2021;82:47-56.
49. Kim T, Samuel EP, Park C, et al. Wearable fabric supercapacitors using supersonically sprayed reduced graphene and tin oxide. *J Alloys Compd*. 2021;856:157902.
50. Wang Z, Zhu M, Pei Z, et al. Polymers for supercapacitors: boosting the development of the flexible and wearable energy storage. *Mater Sci Eng R Rep*. 2020;139:100520.

51. Cheng H, Shapter JG, Li Y, Gao GJ. Recent progress of advanced anode materials of lithium-ion batteries. *Energy Chem.* 2021;57:451-468.
52. Ji X, Xia Q, Xu Y, Feng H, Wang P, Tan Q. A review on progress of lithium-rich manganese-based cathodes for lithium ion batteries. *J Power Sources*. 2021;487:229362.
53. Chen X, Bai YK, Zhao CZ, Shen X, Zhang Q. Lithium bonds in lithium batteries. *Ang Chem Int Ed*. 2020;59:11192-11195.
54. Azam MA, Safie NE, Ahmad AS, Yuza NA, Zulkifli NSAJ. Recent advances of silicon, carbon composites and tin oxide as new anode materials for lithium-ion battery: a comprehensive review. *Energy Storage*. 2021;33:102096.
55. Zhao X, Lehto VP. Ship in bottle synthesis of yolk-shell MnS@hollow carbon spheres for sodium storage. *Nanotechnology*. 2021;32:32.
56. Maia BA, Magalhães N, Cunha E, Braga MH, Santos RM, Correia N. Designing versatile polymers for lithium-ion battery applications: a review. *Polymers*. 2022;14:403.
57. Chen J, Wu J, Wang X, Zhou A, Yang Z. Research progress and application prospect of solid-state electrolytes in commercial lithium-ion power batteries. *Energy Storage Mater*. 2021;35:70-87.
58. Ghadi BM, Yuan M, Ardebili H. Stretchable fabric-based $LiCoO_2$, electrode for lithium ion batteries. *Extreme Mech Lett*. 2019;32:1.
59. Yu S, Xu Q, Tsai CL, et al. Flexible all-solid-state Li-ion battery manufacturable in ambient atmosphere. *ACS Appl Mater Interfaces*. 2020;12:37067-37078.
60. Sang Z, Yan X, Wen L, et al. A graphene-modified flexible SiOC ceramic cloth for high-performance lithium storage. *Energy Storage Mater*. 2020;25:876-884.
61. Joshi B, Samuel E, Kim Y, Yarin AL, Swihart MT, Yoon SS. Progress and potential of electrospinning-derived substrate-free and binder-free lithium-ion battery electrodes. *Chem Eng J*. 2022;430:132876.
62. Garlotta D. A literature review of poly (lactic acid). *J Polym Environ*. 2019;9:63-84.
63. Zhu C, Yang P, Chao D, Mai W, Fan HJ. Heterogeneous nanostructures for sodium ion batteries and supercapacitors. *ChemNanoMat*. 2015;1:458-476.
64. Chen Y, Kang Y, Zhao Y, et al. A review of lithium-ion battery safety concerns: the issues, strategies, and testing standards. *J Energy Chem*. 2021;59:83-99.
65. Allen J. Review of polymers in the prevention of thermal runaway in lithium-ion batteries. *Energy Rep*. 2020;6:217-224.
66. Aktaş A, Kirçiçek Y. Solar Hybrid Systems and Energy Storage Systems. *Solar Hybrid Systems*; Cambridge, MA: Academic Press; 2021:87–125. http://dx.doi.org/10.1016/B978-0-323-88499-0.00005-7
67. Jiang M, Zhang Z, Tang B, et al. Polymer electrolytes for Li-S batteries: polymeric fundamentals and performance optimization. *J Energy Chem*. 2021;58:300-317.
68. Wang Z, Wang X, Sun Z, Li Y, Li J, Shi Y. Enhanced energy storage property of plate-like $Na0.5Bi_4.5Ti_4O15$/poly(vinylidene fluoride) composites through texture arrangement. *Ceram Int*. 2019;45:18356-18362.
69. Zha JW, Zheng MS, Fan BH, Dang ZM. Polymer-based dielectrics with high permittivity for electric energy storage: a review. *Nano Energy*. 2021;89:106438.
70. Vicentini R, Aguiar JP, Beraldo R, et al. Ragone plots for electrochemical double-layer capacitors. *Batter Supercapacitors*. 2021;4:1291-1303.
71. Lee JKY, Chen N, Peng S, et al. Polymer-based composites by electrospinning: preparation & functionalization with nanocarbons. *Prog Polym Sci*. 2018;86:40-84.
72. Maurel A, Armand M, Grugeon S, et al. Poly(ethylene oxide)−LiTFSI solid polymer electrolyte filaments for fused deposition modeling three-dimensional printing. *J Electrochem Soc*. 2020;167:070536.
73. Kumar R, Kumar M, Chohan JS. Material-specific properties and applications of additive manufacturing techniques: a comprehensive review. *Bull Mater Sci*. 2021;44:44.
74. Gulzar U, Glynn C, O'Dwyer C. Additive manufacturing for energy storage: methods, designs and material selection for customizable 3D printed batteries and supercapacitors. *Curr Opin Electrochem*. 2020;20:46-53.
75. Maurel A, Grugeon S, Armand M, et al. Overview on lithium-ion battery 3D-printing by means of material extrusion. *ECS Trans*. 2020;98:3.
76. Goh GD, Yap YL, Tan HKJ, Sing SL, Goh GL, Yeong WY. Process–structure–properties in polymer additive manufacturing via material extrusion: a review. *Crit Rev Solid State Mater Sci*. 2020;45:113-133.
77. Zaarour B, Zhu L, Huang C, Jin X. A mini review on the generation of crimped ultrathin fibers via electrospinning: materials, strategies, and applications. *Polym Adv Technol*. 2020;31:1449-1462.
78. Radacsi N, Nuansing W. *Fabrication of 3D and 4D Polymer Micro- and Nanostructures Based on Electrospinning*. Amsterdam, Netherlands: Elsevier Inc.; 2019:191-229. https://doi.org/10.1016/B978-0-12-816805-9.00007-7
79. Barbosa JC, Pinto RS, Hilliou L, et al. Poly(vinylidene fluoride-trifluoroethylene-chlorofluoroethylene): a new binder for conventional and printable lithium-ion batteries. *ACS Appl Energy Mater*. 2021;4:14129-14140.
80. Pinto RS, Serra JP, Barbosa JC, et al. Direct-ink-writing of electroactive polymers for sensing and energy storage applications. *Macromol Mater Eng*. 2021;306:1.
81. Zhang F, Wu K, Xu X, et al. 3D printing of graphite electrode for lithium-ion battery with high areal capacity. *Energy Technol*. 2021;9:9.
82. Praveen S, Sim GS, Ho CW, Lee CW. 3D-printed twisted yarn-type Li-ion battery towards smart fabrics. *Energy Storage Mater*. 2021;41:748-757.
83. Maurel A, Grugeon S, Fleutot B, et al. Three-dimensional printing of a $LiFePO_4$/graphite battery cell via fused deposition modeling. *Sci Rep*. 2019;9:1.
84. Maurel A, Russo R, Grugeon S, Panier S, Dupont L. Environmentally friendly lithium-terephthalate/polylactic acid composite filament formulation for lithium-ion battery 3D-printing via fused deposition modeling. *ECS J Solid State Sci Technol*. 2021;10:037004.
85. Ghosh K, Ng S, Iffelsberger C, Pumera M. Inherent impurities in graphene/polylactic acid filament strongly influence on the capacitive performance of 3D-printed electrode. *Chem A Eur J*. 2020;26:15746-15753.
86. Arias-Ferreiro G, Ares-Pernas A, Dopico-García MS, Lasagabáster-Latorre A, Abad MJ. Photocured conductive

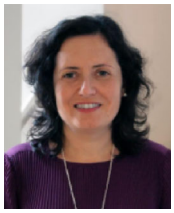
PANI/acrylate composites for digital light processing. Influence of HDODA crosslinker in rheological and physicochemical properties. *Eur Polym J*. 2020;136:109887.
87. Zhou M, Bahi A, Zhao Y, et al. Enhancement of charge transport in interconnected lignin-derived carbon fibrous network for flexible battery-supercapacitor hybrid device. *Chem Eng J*. 2021;409:128214.
88. Barbosa JC, Correia DM, Fidalgo-Marijuan A, et al. Sustainable lithium-ion battery separators based on poly(3-hydroxybutyrate-co-hydroxyvalerate) pristine and composite electrospun membranes. *Energy Technol*. 2022;10:2100761.
89. Cárdenas-Martínez J, España-Sánchez BL, Esparza R, Ávila-Niño JA. Flexible and transparent supercapacitors using electrospun PEDOT:PSS electrodes. *Synth Met*. 2020;267:116436.
90. Li X, Chen X, Zhao Y, et al. Flexible all-solid-state supercapacitors based on an integrated electrode of hollow N-doped carbon nanofibers embedded with graphene nanosheets. *Electrochim Acta*. 2020;332:135398.
91. Cheng M, Jiang Y. 3D-printed solid-state electrolytes for electrochemical energy storage devices. *J Mater Res*. 2021;36:4547–4564.
92. Liu Z, Tian X, Liu M, et al. Direct ink writing of $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$-based solid-state electrolytes with customized shapes and remarkable electrochemical behaviors. *Small*. 2021;17:1.
93. Zhang Q, Zhou J, Chen Z, et al. Direct ink writing of moldable electrochemical energy storage devices: ongoing progress, challenges, and prospects. *Adv Eng Mater*. 2021;23:1.
94. Tagliaferri S, Panagiotopoulos A, Mattevi C. Direct ink writing of energy materials. *Mater Adv*. 2021;2:540-563.
95. Wickramasinghe S, Do T, Tran P. FDM-based 3D printing of polymer and associated composite: a review on mechanical properties, defects and treatments. *Polymers*. 2020;12:1529.
96. Meng F, Zhang M, Huang J, Lu WF, Xue JM, Wang H. Photonic crystals: integration of polymer synthesis and self-assembly for controlled periodicity and photonic properties. *Adv Funct Mater*. 2021;31:2005819.
97. Nath SD, Nilufar S. Polyacrylamide based polymers: smart materials used in wastewater treatment. *Polymers*. 2020;12:1-107.
98. Arias-ferreiro G, Ares-pernas A, Lasagabáster-latorre A, et al. Printability study of a conductive polyaniline/acrylic formulation for 3D printing. *Polymers*. 2021;13:2068.
99. Wang XX, Yu GF, Zhang J, Yu M, Ramakrishna S, Long YZ. Conductive polymer ultrafine fibers via electrospinning: preparation, physical properties and applications. *Prog Mater Sci*. 2021;115:100704.
100. Umiati NAK, Kadarisman VGS, Subagio A, Wandono K. A simple homemade electrospinning for nanoscale fibres production. *E3S Web Conf*. 2019;125:10.
101. Senthil Muthu Kumar T, Senthil Kumar K, Rajini N, Siengchin S, Ayrilmis N, Varada Rajulu A. A comprehensive review of electrospun nanofibers: Food and packaging perspective. *Compos Part B Eng*. 2019;175:107074.
102. Robert Ilango P, Peng S. Electrospinning techniques for Li, Na and K-ion batteries. *Curr Opin Electrochem*. 2019;18:106-112.
103. Liao M, Ye L, Zhang Y, Chen T, Peng H. The recent advance in fiber-shaped energy storage devices. *Adv Electron Mater*. 2019;5:1.
104. Lyu W, Zhang W, Liu H, et al. Conjugated microporous polymer network grafted carbon nanotube fibers with tunable redox activity for efficient flexible wearable energy storage. *Chem Mater*. 2020;32:8276-8285.
105. Ren J, Zhang Y, Bai W, et al. Elastic and wearable wire-shaped lithium-ion battery with high electrochemical performance. *Ang Chem Int Ed*. 2014;53:7864-7869.
106. Kwon YH, Woo SW, Jung HR, et al. Cable-type flexible lithium ion battery based on hollow multi-helix electrodes. *Adv Mater*. 2012;24:5192-5197.
107. Fu Y, Cai X, Wu H, et al. Fiber supercapacitors utilizing pen ink for flexible/wearable energy storage. *Adv Mater*. 2012;24:5713-5718.
108. Yu Z, Thomas J. Energy storing electrical cables: integrating energy storage and electrical conduction. *Adv Mater*. 2014;26:4279-4285.
109. Razaq A, Bibi F, Zheng X, Papadakis R, Hassan S, Jafri M. Review on graphene-, graphene oxide-, reduced graphene oxide-based flexible composites: from fabrication to applications. *Materials*. 2022;15:1.
110. Cheng H, Li Q, Zhu L, Chen S. Graphene fiber-based wearable supercapacitors: recent advances in design, construction, and application. *Small Methods*. 2021;5:1.
111. Khudiyev T, Lee JT, Cox JR, et al. 100 m long thermally drawn supercapacitor fibers with applications to 3D printing and textiles. *Adv Mater*. 2020;32:1.
112. Zhang L, Liu D, Wu ZS, Lei W. Micro-supercapacitors powered integrated system for flexible electronics. *Energy Storage Mater*. 2020;32:402-417.
113. Alameen A, Jin T, Xue C, Ma X, Du X, Hao X. Flexible all-solid-state supercapacitor based on polyhedron C-ZIF-8/PANI composite synthesized by unipolar pulse electrodeposition method. *J Solid State Electrochem*. 2020;25:777-787.
114. Meng W, Xia Y, Ma C, Du X. Electrodeposited polyaniline nanofibers and MoO_3 nanobelts for high-performance asymmetric supercapacitor with redox active electrolyte. *Polymers*. 2020;12:2303.
115. Li A, Xu L, Li CM, Qian Y. Mesh-like LiZnBO 3/C composites as a prominent stable anode for lithium ion rechargeable batteries. *J Mater Chem A*. 2016;4:5489-5494.
116. Lopez J, Gonzalez R, Ayala J, et al. Centrifugally spun TiO_2/C composite fibers prepared from TiS_2/PAN precursor fibers as binder-free anodes for LIBS. *J Phys Chem Solid*. 2021;149:109795.
117. Li H, Xi J, Donaghue AG, et al. Synthesis and catalytic performance of polydopamine supported metal nanoparticles. *Sci Rep*. 2020;10:1.
118. Sumdani MG, Islam MR, Yahaya ANA, Safie SI. Recent advancements in synthesis, properties, and applications of conductive polymers for electrochemical energy storage devices: a review. *Polym Eng Sci*. 2021;62:269-303.
119. Behera R, Elanseralathan KJ. A review on polyvinylidene fluoride polymer based nanocomposites for energy storage applications. *Energy Storage*. 2022;48:103788.

120. Lasrado D, Ahankari S, Kar K. Nanocellulose-based polymer composites for energy applications—a review. *J Appl Polym Sci*. 2020;137:1.
121. Wua X, Zhenga Y, Li W, et al. Solid electrolytes reinforced by infinite coordination polymer nano-network for dendrite-free lithium metal batteries. *Energy Storage Mater*. 2021;41:436-447.
122. Wavhal BA, Ghosh M, Sharma S, Kurungot S, Asha SK. A high-voltage non-aqueous hybrid supercapacitor based on the N2200 polymer supported over multiwalled carbon nanotubes. *Nanoscale*. 2021;13:12314-12326.
123. Mirabedini A, Lu Z, Mostafavian S, Foroughi J. Triaxial carbon nanotube/conducting polymer wet-spun fibers supercapacitors for wearable electronics. *Nanomaterials*. 2021;11:1.
124. Liu G, Chen X, Liu J, et al. Fabrication of PEDOT:PSS/rGO fibers with high flexibility and electrochemical performance for supercapacitors. *Electrochim Acta*. 2021;365:137363.
125. Teng W, Zhou Q, Wang X, et al. Enhancing ions/electrons dual transport in rGO/PEDOT:PSS fiber for high-performance supercapacitor. *Y*. 2022;189:284-292.
126. Song J, Sui Y, Zhao Q, et al. A reinforced concrete structure rGO/CNTs/Fe2O3/PEDOT:PSS paper electrode with excellent wettability and flexibility for supercapacitors. *New J Chem*. 2021;45:14483-14494.
127. Huang H, Zhao Y, Cong T, et al. Flexible and alternately layered high-loading film electrode based on 3D carbon nanocoils and PEDOT:PSS for high-energy-density supercapacitor. *Adv Funct Mater*. 2022;1:2110777.
128. Li S, Huang J, Wang J, Han K. Micro-sized porous silicon@PEDOT with high rate capacity and stability for Li-ion battery anode. *Mater Lett*. 2021;293:129712.
129. Zhu H, Sun X, Yang H, et al. Polydopamine-derived nitrogen-doped carbon-coated NiS nanoparticles as a battery-type electrode for high-performance supercapacitors. *Ceram Int*. 2021;47:9332-9341.
130. Tian J, Xue Y, Yu X, Pei Y, Zhang H. Co_3O_4 nanorods with prevalent oxygen-vacancies confined by PDA-RGO nanosheets for excellent performances in supercapacitors. *J Solid State Chem*. 2021;297:122076.
131. Wang C, He T, Cheng J, Guan Q, Wang B. Bioinspired interface design of sewable, weavable, and washable fiber zinc batteries for wearable power textiles. *Adv Funct Mater*. 2020;30:1.
132. Zhang M, Nautiyal A, Du H, et al. Polypyrrole film based flexible supercapacitor: mechanistic insight into influence of acid dopants on electrochemical performance. *Electrochim Acta*. 2020;357:136877.
133. Lima N, Baptista AC, Faustino BMM, Taborda S, Marques A, Ferreira I. Carbon threads sweat-based supercapacitors for electronic textiles. *Sci Rep*. 2020;10:1.
134. Hao B, Deng Z, Bi S, et al. In situ polymerization of pyrrole on CNT/cotton multifunctional composite yarn for supercapacitors. *Ionics (Kiel)*. 2021;27:279-288.
135. Li X, Xie X, Lv R, Na B, Wang B, He Y. Nanostructured polypyrrole composite aerogels for a rechargeable flexible aqueous Zn-ion battery with high rate capabilities. *Energ Technol*. 2019;7:1.
136. Chu X, Zhao X, Zhou Y, et al. An ultrathin robust polymer membrane for wearable solid-state electrochemical energy storage. *Nano Energy*. 2020;76:105179.
137. Jiang Q, Shang Y, Sun Y, et al. Flexible and multi-form solid-state supercapacitors based on polyaniline/graphene oxide/CNT composite films and fibers. *Diamond Relat Mater*. 2019;92:198-207.
138. Taravati Ahmad, P.; Jaleh, B.; Khazalpour, S.; Gharehbaghi, R.; Varma, R. S *J Mater Sci Mater Electron*. 2021.
139. Huang Z, Ji Z, Feng Y, Wang P, Huang Y. Flexible and stretchable polyaniline supercapacitor with a high rate capability. *Polym Int*. 2021;70:437-442.
140. Reyes C, Somogyi R, Niu S, et al. Three-dimensional printing of a complete lithium ion battery with fused filament fabrication. *ACS Appl. Energy Mater*. 2018;1:5268.
141. Nie W, Liu L, Li Q, et al. A wearable fiber-shaped supercapacitor based on a poly(lactic acid) filament and high loading polypyrrole. *RSC Adv*. 2019;9:19180-19188.
142. Jellett C, Ghosh K, Browne MP, Urbanová V, Pumera M. Flexible graphite–poly(lactic acid) composite films as large-area conductive electrodes for energy applications. *ACS Appl Energy Mater*. 2021;4:6975-6981.
143. He K, Wong TC, Lau GS. Ionic liquid-based high-voltage flexible supercapacitor for integration with wearable human-powered energy harvesting system. *J Appl Electrochem*. 2019;49:79-86.
144. Chen R, Yang Y, Huang Q, et al. A multifunctional interface design on cellulose substrate enables high performance flexible all-solid-state supercapacitors. *Energy Storage Mater*. 2020;32:208-215.
145. Haghshenas M, Mazloum-Ardakani M, Tamaddon F, Nasiri A. $CoFe_2O_4$@methyl cellulose core-shell nanostructure and their hybrids with functionalized graphene aerogel for high performance asymmetric supercapacitor. *Int J Hydrogen Energy*. 2021;46:3984-3995.
146. Charkhesht V, Yürüm A, Alkan Gürsel S, Yarar Kaplan B. Titania-based freestanding electronically conductive electrospun anodes with enhanced performance for Li-ion batteries. *ACS Appl Energy Mater*. 2021;4:13922-13931.
147. Wang J, Hao X, Wang R, et al. A novel functional polymeric binder for silicon anodes in lithium-ion batteries. *J Phys Conf Ser*. 2021;2021:012017.
148. Jiang W, Yang X, Deng J, Zhang J, Zhang G. Polydopamine-based materials applied in Li-ion batteries: a review. *J Mater Sci*. 2021;56:19359-19382.
149. Zhu M, Jia X, Li Y, Zhao C, Chao D, Wang C. A cytocompatible conductive polydopamine towards electrochromic energy storage device. *Electrochim Acta*. 2021;374:374.
150. Chen J, Wang Y, Chen W. Superior capacitive energy storage capability in polymer composites induced by polydopamine-coated paraelectric platelets. *J Mater Sci*. 2021;56:9395-9407.
151. Sheng Y, Zhang X, Ye H, Liang L, Xu L, Wu H. Improved energy density in core–shell poly(dopamine) coated barium titanate/poly(fluorovinylidene-co-trifluoroethylene) nanocomposite with interfacial polarization. *Colloids Surfaces A Physicochem Eng Asp*. 2020;585:124091.
152. Zheng X, Yao L, Qiu Y, Wang S, Zhang K. Core–sheath porous polyaniline nanorods/graphene fiber-shaped supercapacitors with high specific capacitance and rate capability. *ACS Appl Energy Mater*. 2019;2:4335-4344.

153. Ghosh K, Ng S, Iffelsberger C, Pumera M. 2D MoS_2/carbon/polylactic acid filament for 3D printing: photo and electrochemical energy conversion and storage. *Appl Mater Today*. 2022;26:101301.
154. Vaghasiya JV, Mayorga-Martinez CC, Pumera M. Smart energy bricks: Ti3C2@polymer electrochemical energy storage inside bricks by 3D printing. *Adv Funct Mater*. 2021;31:31.
155. Redondo E, Muñoz J, Pumera M. Green activation using reducing agents of carbon-based 3D printed electrodes: Turning good electrodes to great. *Carbon*. 2021;175:413.
156. Tafete GA, Abera MK, Thothadri GJ. Review on nanocellulose-based materials for supercapacitors applications. *Energy Storage*. 2022;48:103938.

AUTHOR BIOGRAPHIES

Silvia Lage-Rivera completed her degree in Chemical Process Engineering in USC, Spain (2019). She is pursuing her PhD in applied physics. Her current research is focused on the research of new polymeric materials with electrical properties to be used in energy storage devices.



Ana Ares-Pernas has been an associate professor since 2012 in Engineering Degree in Industrial Design and Product Development. She has worked in the polymers group, since more than 20 years, specializing in the rheology, processing, and structure-property relationship of polymers. Last years, she has been working in conducting polymers and polymers for additive manufacturing. In addition, she has been the plastics laboratory quality manager since more than 10 years.

María-José Abad has been an associate professor in UDC since 2010. She works in Polymers Group, specializing on electrical properties, rheology, processing, and structure-property relationship of polymers. She has been technical manager of the plastics laboratory for more than 20 years. Since 2011, her research work is focused on the synthesis of intrinsically conductive polymers, as polyaniline, and the development of conducting polymer composites for 3D printing. Over the years, she has combined frontier academic research with industrial R&D with industrial partners in polymer science and technology.

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