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Development of New Nanostructured Electrodes for Electrochemical Conversion: Energy and Fuels from the Environment

Giulia Massaglia and Marzia Quaglio

Additional information is available at the end of the chapter

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Abstract

During the last decade, carbon-based nanofibers emerged as an important class of materials for the fabrication of electrodes for electrochemical energy conversion. Indeed carbon-based nanofibers combine high electrochemical stability and high porosity to high mechanical flexibility and low weight, resulting in a unique and versatile material for the design and fabrication of energy-related devices. This chapter aims to show and analyze new nanostructured materials, obtained by electrospinning technique, in order to design 3D arrangement of the electrodes and to improve the energy efficiency of energy production devices. Indeed, the design of new 3D nanostructured electrodes enhances the energy efficiency of these devices, optimizing the energy production, obtained by new renewable energy technologies. The chapter is focused on those devices able to generate power output through the electrochemical conversion of different fuels, like wastes, and environmental compounds, such as CO₂.

Keywords: carbon nanofibers, electrospinning, carbon-based electrodes, energy conversion devices, energy storage devices

1. Introduction

Electrospinning is a unique process for the fabrication of 1D nanomaterials. During the last decades, it gained progressive interest, demonstrating huge potential in the different scientific areas. Especially in the field of energy and electrochemical energy conversion (EEC), electrospinning has a leading role among the techniques for the fabrication of nanomaterials.

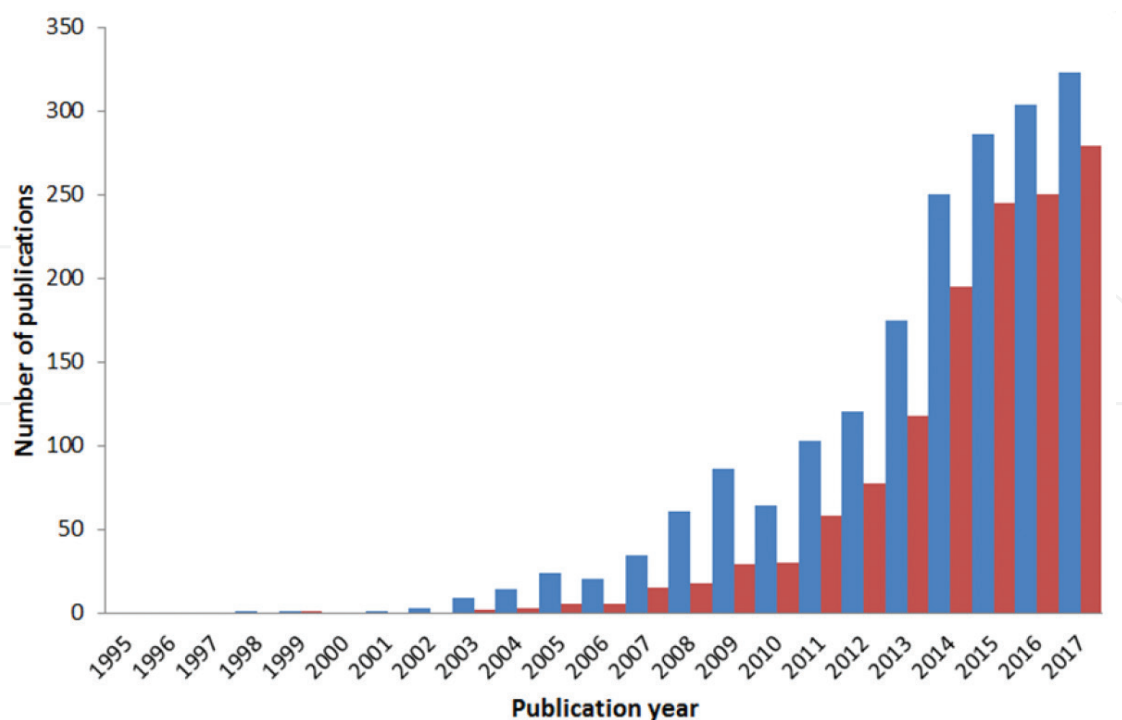


Figure 1. Number of publications discussing carbon-based nanofibers by electrospinning in blue, and in red the number of works specifically related to energy is reported (source SCOPUS).

Indeed, it offers the possibility to fabricate 1D nanostructures with good control of the nanofiber morphology and of their arrangement in the final mats.

In EEC devices, carbon-based nanofibers have attracted particular interest for the design of high-performing electrodes. They combine high electrochemical stability to unique mechanical properties, exhibiting high surface area to volume ratio.

The high interest on carbon-based nanofibers by electrospinning is evidently analyzed in **Figure 1**, in which the number of works on this topic, published during the last 20 years, is reported by the blue columns. What is even more interesting is that a significant number of those works discussed the application in energy of carbon nanofibers, as described by the red columns.

This chapter analyzes the fabrication of carbon-based nanofibers by electrospinning, discussing their formation from different carbon precursors proposed in the literature, presenting the processing of nanofibrous electrodes for EEC and reporting key examples of their application in different EEC systems.

2. Electrochemical energy conversion

Electrochemical energy conversion (EEC) refers to the conversion of chemical energy into electrical energy by the proper control of reduction-oxidation (redox) reactions. By processes of this kind, it is possible to convert chemical energy, trapped in chemical bonds of different molecules acting like fuels, into electrical energy as in fuel cells (FC) [1], or to harvest solar energy of photons thanks to the presence of proper molecules decorating the surface of a

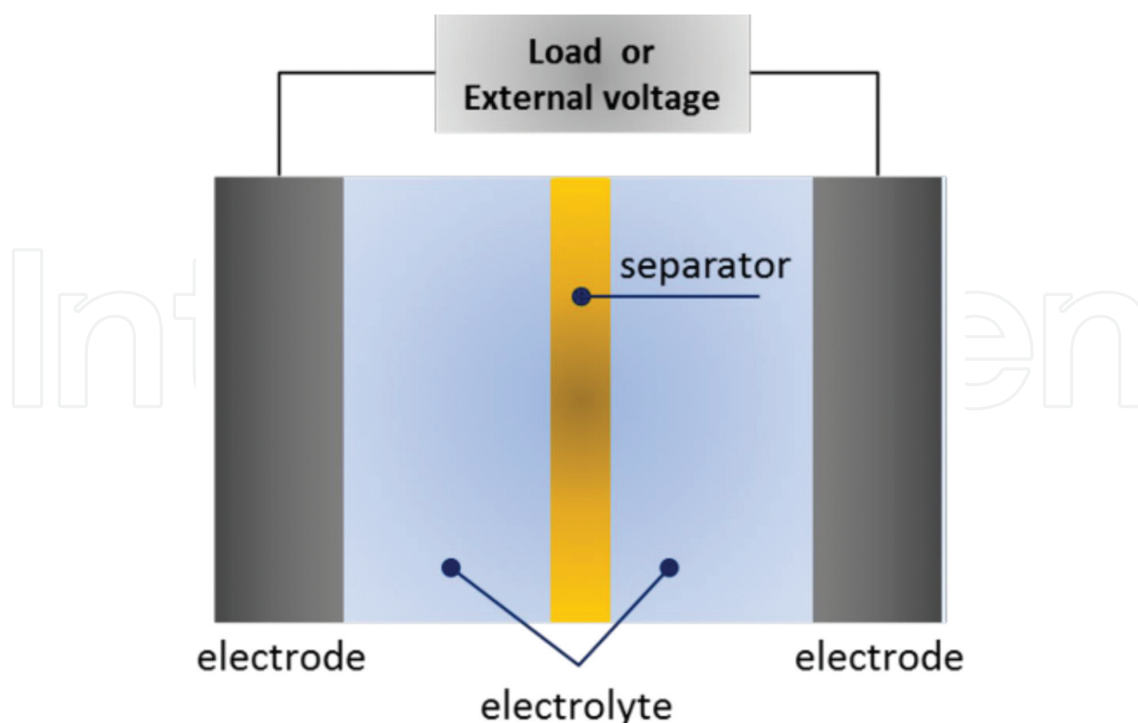


Figure 2. Schematic representation of an electrochemical reactor.

semiconducting oxide as in dye-sensitized solar cells (DSSC) [2]. EEC also permits to store energy for its further use as in supercapacitors, by the creation of a double-layered charges, [3, 4] and in Li-ion batteries, by the so-called intercalation process [5]. Moreover, EEC can be associated to redox reactions, induced to obtain new molecules, able to efficiently store the starting energy into their chemical bonds. Interesting examples are electrocatalytic water splitting for H_2 production, [6] or CO_2 photoelectrochemical reduction [7].

From a general point of view, all these electrochemical reactors have a common structure, as reported in **Figure 2**. Indeed, they all are made of two electrodes, that is, anode and cathode, a liquid (or semisolid) electrolyte, eventually containing a separator. Actually, the optimization of the different EEC systems requires specific strategies to properly control the crucial reactions and processes occurring inside them. General agreement exists in this field on the key role played by the material constituting the electrodes. For each EEC system, the electrode material needs to satisfy some requirements. It must

- be chemically robust, so as to sustain the electrochemical reaction for long time without degrading or limiting the reaction efficiency;
- be high electrically conductive;
- expose high surface area to volume ratio, so expose high area to favor the reactions;
- have high durability over time;
- have high mechanical strength, possibly combined to good mechanical flexibility.

During the last decade, carbon-based materials demonstrated to be the best candidate to fulfill all the requirements, especially when they are nanostructured. In this scenario, carbon-based nanofibers have started to be explored in the field of EEC, showing a tremendous potential to contribute to the further development of this area.

3. Carbon-based nanofibers by electrospinning

Electrospinning process ensures the formation of carbon nanofibers, starting from a polymeric solution and applying successively a proper post-process, typically a thermal treatment, known as pyrolysis process, conducted at high temperature and under an inert atmosphere [8]. The selection of the polymeric precursor with a carbonization yield plays a crucial role in order to obtain final carbon-based nanofiber mats. One of the main advantages, offered by electrospinning technique, is the possibility to obtain several nanostructures, such as hollow nanofibers, porous and dense nanofibers, by using different tools. The electrospinning setup is basically characterized by three parts: (1) the spinneret that hosts the needle representing the first electrode; (2) the counter electrode, also named collector, which is the second electrode and it ensures the collection of dried nanofiber mats; and (3) high voltage supply [9–12]. As sketched in **Figure 3**, the high

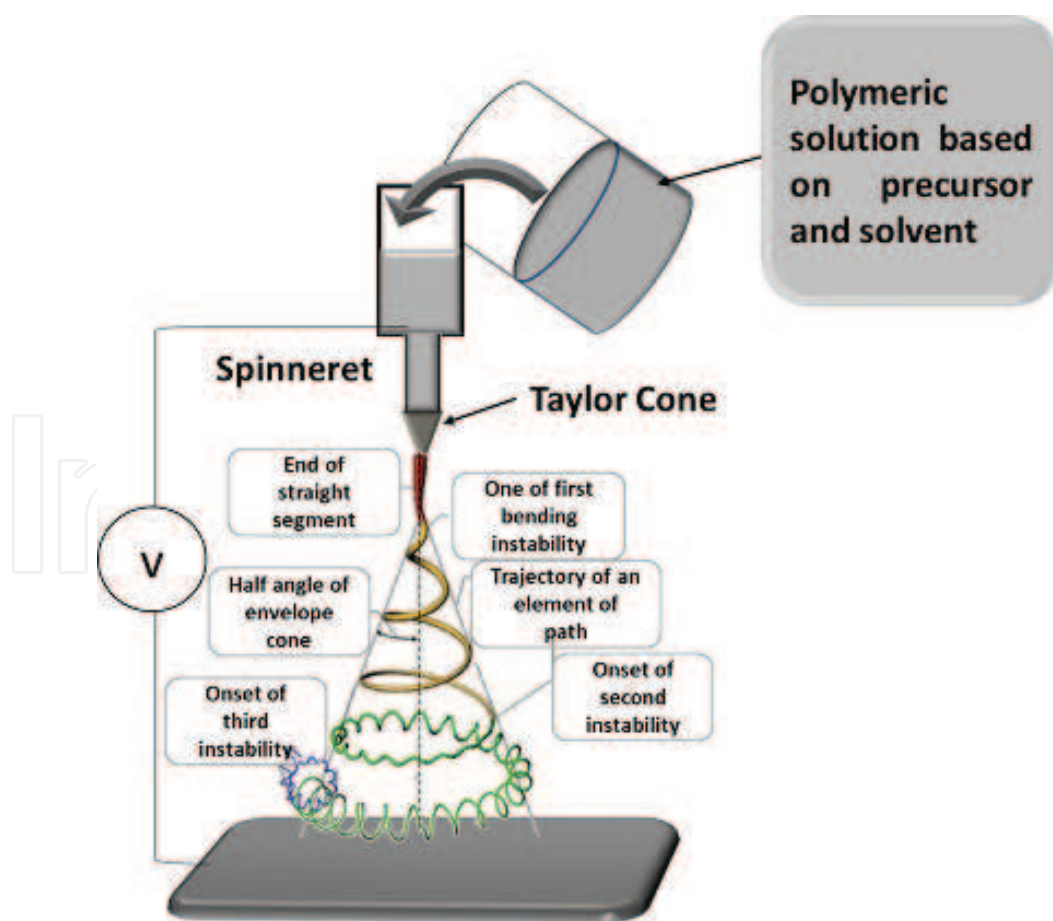


Figure 3. Scheme of the electrospinning process together with the representation of bending instabilities achieved during the process. Reprinted with the permission from (Polymer, 2008, 49, 2387–2425) Copyright (2008) Elsevier.

voltage (in the range between 0 and 30 kV) is applied to induce charges distribution inside the polymeric drop that is shaped at the tip of the needle. The interaction between all charges generates a repulsive force, which typically increases as the voltage value grows. Indeed, as voltage progressively increases, the spherical shape of the drop is stretched, assuming a conical shape, named Taylor cone. When the applied voltage overcomes the threshold value, the repulsive force overcomes the surface tension of solution, inducing the ejection of charged polymeric jet.

Since during the process, both bending instabilities and solvent evaporation induce the stretching of the charged polymeric jet, leading to provide the deposition of nanofibers with diameters in the order from few nanometers to some micrometers, the definition of working distance is quite important [13–15]. The working distance is defined as the distance between the tip of needle and the counter electrode and it is directly correlated with the possibility to collect on the counter electrode a dried nanofiber mat. All the process parameters play a crucial role to tune the morphological properties of the nanofibers. Furthermore, the subdivision of these parameters in three main classes is completely known:

- i. Polymeric solution parameters, such as viscosity, electrical conductivity, surface tension, concentration and polymer molecular weight;
- ii. Process parameters, as applied voltage, working distance, flow rate and strength electric field, defined as the ratio between the voltage and the working distance;
- iii. Environmental parameters, such as room temperature and humidity.

Moreover, the spinnability of the polymeric solution is strictly correlated with the solution parameters. In order to obtain the formation of a continuous charged polymeric jet during the process, the solution viscosity must be in the range (Eq. 1) [16–18]:

$$0.02 \leq \eta \leq 200 \text{ Pa} \cdot \text{s} \quad (1)$$

When the viscosity value, (η (Pa*s)), is lower than 0.1 Pa*s, charged droplets are formed during the process, giving rise to electrospray process. On the contrary, when the solution viscosity is higher than 2 Pa*s, the formation of a continuous charged polymeric jet occurred, leading thus to collect dried nanofiber mats. Different works in the literature demonstrate the direct correlation between the solution viscosity and the uniform morphological properties, characterizing the nanofiber mat [16]. It is possible to define a direct correlation between polymer concentration and solution viscosity: higher is the polymer concentration, higher is the solution viscosity. When the polymer concentration is low, thinner nanofiber mats are collected on the counter electrode.

Regarding the second class of parameters, the flow rate and working distance affect the morphological properties of final nanofibers. High flow rate values, indeed, induce the formation of nanofibers, characterized by a no uniform diameter distribution and by a large number of defects. Whereas low flow rate values cause the formation of the Taylor cone inside the needle, leading to the formation of no continuous charged polymeric jet and the collection of beads nanostructured into the mats. Since the evaporation of the solvent can depend on the working distance, its value influences the collection of the final dried nanofiber mats.

3.1. The reference process: Poly (acrylonitrile) as the carbon source

As deeply investigated in the literature [8, 19], the main polymeric precursor used in order to obtain carbon-based nanofibers is Poly (acrylonitrile) (PAN). The polymer chain of PAN is represented in **Figure 4**.

PAN is selected as precursor thanks to its properties, such as high carbonization yield, high melting polymer and high content of nitrogen, leading to the self-induced nitrogen doping into the final nanofiber mats, modulating properly the heating treatment [19]. Different works in the literature investigate the role of nitrogen in order to optimize the carbon-based nanofibers, designing new electrode to improve the overall performance of electrochemical devices. In particular, the so-called activated carbon-based nanofibers (ACNFs) are obtained by applying successive chemical treatments (e.g. ammonia treatments, oxidation treatment in nitric acid and so on) on carbon nanofibers after the thermal treatment conducted at temperatures higher than 100°C [20]. Whereas, PAN nanofibers can show a self-induced nitrogen doping, when the pyrolysis treatment is conducted at low temperature values, in the range from 600–900°C. In order to obtain a final polymeric solution suitable for electrospinning, the most common polymeric mixture is based on PAN dissolved in an organic solvent, as Dimethylformamide (N-N DMF). Different works in the literature investigate the correlation between all involved electrospinning parameters and the morphological properties of PAN nanofibers [8, 21]. Therefore, Yordem et al. [8] demonstrate that the working distance results to be the main parameter, which can be influenced by the diameter distribution in the range of several nanometers. PAN nanofibers can be obtained by starting from a polymeric solution, containing a low PAN concentration (in the range 8–10 wt%) and applying a voltage value among 10–20 kV.

The pyrolysis treatment is the heat treatment, carried out in order to transform the PAN nanofiber mats in carbon nanofibers (CNFs). Liu et al. [22] showed the pyrolysis treatment, divided into three main steps: (i) the oxidative stabilization; (ii) the carbonization; and (iii) the graphitization. All these steps should be implemented in order to maintain the nanostructures during the conversion of PAN fibers into CNFs. Among all these steps, the most important and complex stage results to be the oxidative stabilization. This step plays a crucial role in the definition of carbon nanofiber structures and involves several chemical reactions, such as cyclization, dehydrogenation, aromatization, oxidation and crosslinking [23, 24]. The oxidative stabilization occurred in air at temperature lower or equal to 280°C and during this step, the $C \equiv N$ bonds, characterizing the polymeric chains, is turned into $C = N$, leading thus to the

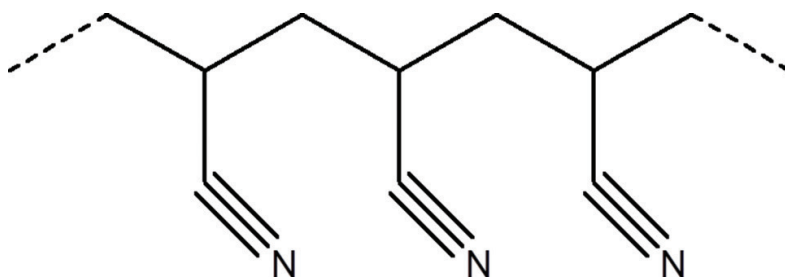


Figure 4. Molecular chain of polymer polyacrylonitrile.

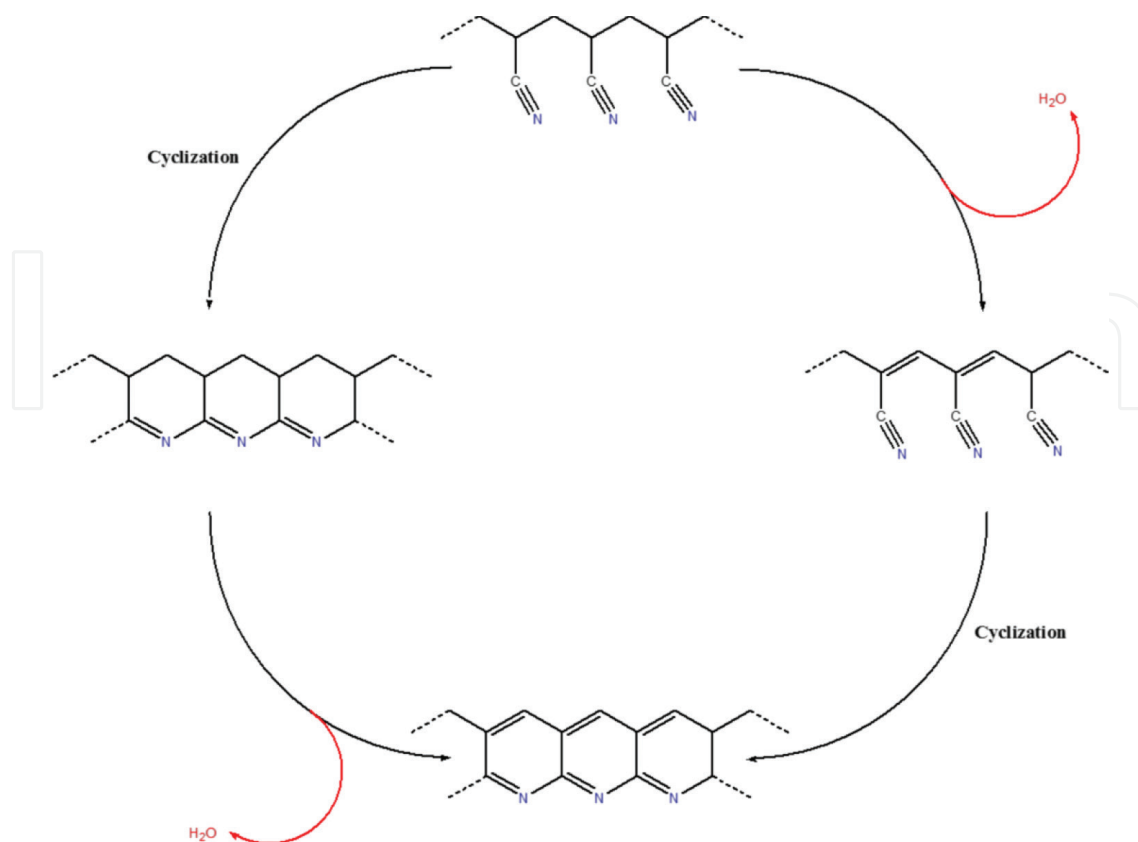


Figure 5. Scheme of the two main reactions occurred during the oxidative stabilization: Cyclization and dehydrogenation, which induces the formation of a water molecule.

crosslinking between PAN molecules and the thermal stabilization of the nanostructures [25]. The main reactions, occurred during this step, are dehydrogenation and cyclization reactions, as sketched in **Figure 5**.

In particular, the dehydrogenation involves the formation of double bonds between nitrogen and carbon atoms and successively the removal of water molecules. Whereas the cyclization is the reaction able to create the ring configuration in the main chain. Indeed, the nitrile groups react with each adjacent group, originating then stable polymeric structure. Once obtained a nanostructured material thermally stable, the following steps of carbonization and graphitization are carried out. Typically, both of the two steps are conducted under inert atmosphere (using argon or nitrogen flow) at high temperature values. The carbonization step is occurred at temperature higher than 900°C and during this phase, the ring structure starts to arrange itself to get the formation of small size graphene sheets. In particular, a molecule of HCN broke out and a reduction of nitrogen content in the main chain takes place. The last graphitization step is conducted for temperature higher than 1000°C ($1000^{\circ}\text{C} < T < 3000^{\circ}\text{C}$) in order to convert the majority of PAN precursor into a carbon structure, ensuring thus the formation of larger graphitic ordered sheets. Although the formation of uniform CNFs mats, starting from PAN as precursor, results to be difficult, the final CNFs show unusual properties, thanks to their high surface area ratio to volume and high porosity webs, making them suitable to design new nanostructured electrodes.

3.2. Other carbon precursors

The class of polymers, reported in **Table 1**, which can be used as precursor in order to obtain carbon-based nanofibers, turn out to be restricted. Theoretically, the carbon backbone ensures the possibility to convert that polymer precursor in a carbon-based material.

One of the most interesting possibilities is the selection of a natural polysaccharide, such as cellulose, chosen as carbon precursor. Deng et al. [26] fabricated CNFs by using nano-sized cellulosic precursors. The nanofibers, obtained by electrospinning of a polymeric solution based on cellulose acetate, were then left in a solution of 0.5 M NaOH dissolved in ethanol to obtain regenerate cellulose-based nanofibers. Subsequently, a pyrolysis treatment was carried out through two steps, converting thus cellulose-based nanofibers into CNFs. The first step is conducted in air at 240°C in order to stabilize the nanostructure, while the carbonization (second step) is obtained by varying the temperature in the range from 800–2200°C under argon flow. In this work, it was possible to observe that the diameters decrease with the increasing of the heating temperature. In particular, the diameters varied from 430 to 200 nm, when the heating temperature is close to 2200°C. These obtained CNFs show an improvement of mechanical resistances, due to their high surface area and small diameter distribution. Moreover, the yield of carbonization of cellulose is ensured by the possibility to obtain a graphitic-like nanostructure starting from 1500°C.

Different synthetic polymers can be used as precursors for carbonization: polyimide (PI), poly(vinyl alcohol) (PVA) and poly(vinyliden fluoride) (PVDF). Many works in the literature investigate the formation of PI nanofibers [27–30], by providing three different steps: (i) preparation of polymeric solution based on polyamic acid (PAA); (ii) electrospinning of this polymeric solution and (iii) imidization of the PAA nanofiber mats. The imidization process is carried out in N₂ atmosphere; during this process two heating phases are implemented: the first is conducted at 150°C for 40 min (heating rate equal to 5°C min⁻¹) and the second one at 280°C for 40 min (heating rate is 2°C min⁻¹) [27]. The carbonization process was conducted at a temperature of 1000°C with a heating rate of 10°C min⁻¹ in inert atmosphere [30, 31]. Different approaches were investigated in order to induce the graphitization of the samples [31] and/or to create a N₂ doping to functionalize the nanofiber mats [30]. Indeed, Yang et al. [31] sandwiched the carbonized PI nanofibers into graphite plates and treated them at 2200°C in He atmosphere. Whereas Kim et al. [30], in order to activate the carbon-based nanofibers after the carbonization process and thus optimize the materials as supercapacitors, implemented a heating treatment at temperature in the range from 650–800°C with a 40%vol steam in the nitrogen. PAA concentration or viscosity solution are the two main parameters that can influence the morphological properties of PI nanofibers [32], as represented in **Figure 6**. The diameters of PI nanofibers vary in the range between some tens and several hundreds nanometers [8]. In order to tune the morphological properties of final carbon nanofibers and their porosity distribution, it is important to underline that the diameter values decrease during the imidization process and the carbonization treatment [31].

The thermoplastic polymer PVDF is used as carbon precursor thanks to its intrinsic properties, which ensure the formation of a continuous charged polymeric jet during the electrospinning, avoiding as much as possible the instauration of nano-droplets during the process [33].

Electrospun carbon-based nanofibers			
Polymeric precursors	Pyrolysis process	Parameters involved in nanofibers morphology	References
PAN dissolved in N-N DMF, used as solvent	Oxidative stabilization conducted in air at T = 280°C Carbonization step conducted under inert atmosphere at T ≥ 900°C Graphitization step conducted under inert atmosphere at 100°C < T < 3000°C	Working distance Polymer concentration Voltage applied in the range from 10 to 20 kV	[8, 20–25]
Nano-sized Cellulosic Precursor	In air at T = 240°C Carbonization step conducted under inert atmosphere at two temperatures: T1 = 800°C and T2 = 2200°C	Heating temperature: average diameters vary in the range from 430 to 200 nm;	[26]
PI nanofibers obtained by starting from a solution based on PAA	Imidization process: in N ₂ T ₁ = 150°C(50 min); T ₂ = 280°C (40 min) Carbonization step: inert atmosphere T = 1000°C	PAA concentration Viscosity solution The diameters of PI nanofibers decrease during imidization process	[8, 27–31]
PVDF nanofibers	Oxidative stabilization process in air at T = 400°C Carbonization process in N ₂ flow is conducted at T = 1000°C	Polymer concentration: higher is the polymeric concentration, higher is the diameter values	[33]
Porous nanofibers obtained starting from a polymeric solution based on PVDF and PEO dissolved in DMF	Oxidative stabilization process in air at T = 400°C Carbonization process in N ₂ flow is conducted at T = 1000°C	Higher is the molecular weight of PEO and its concentration, higher is the pore distribution inside the mat and on nanofibers surface.	[34]
PVA nanofibers	Carbonization process is implemented at low temperature T = 500°C under flow of argon and hydrogen	pH of polymeric solution: diameters increase as the basic pH increases: pH is more acid the formation of charged droplets occurred	[35, 36]
Core-shell and hollow carbon-based Nanofibers			
Polymeric precursors	Pyrolysis process	Hollow Carbon-based nanofibers	References
PAN dissolved in N-N DMF, used as shell	Oxidative stabilization conducted in air at T = 250°C	Hollow nanofibers show an external diameter equal to 7 μm and the internal diameter is close to 2 μm	[37–39]
PMMA, mixed in a solvent of DMF/acetone, used as core	Carbonization step conducted under inert atmosphere at T = 1100°C		

Table 1. Summary of process parameters involved during the electrospinning process and the pyrolysis process, in order to establish a correlation with the morphological properties of carbon-based nanofibers.

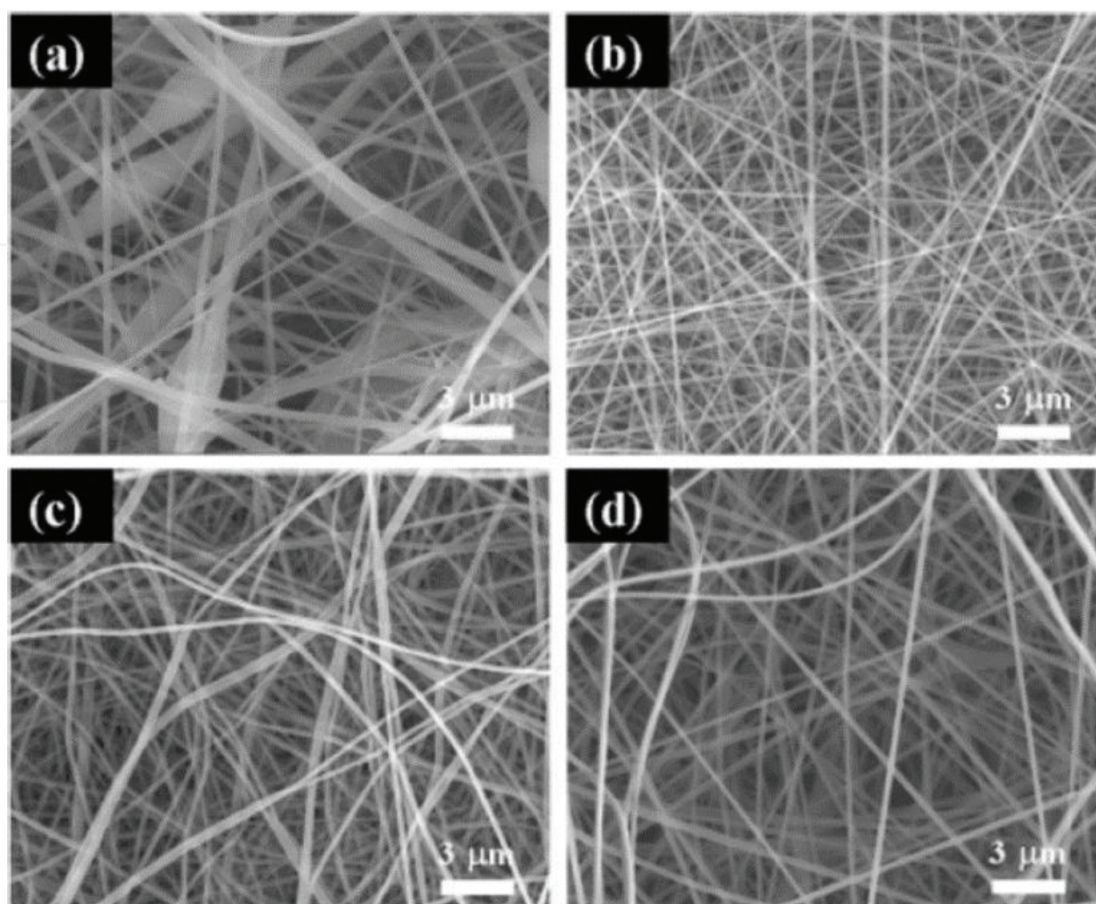


Figure 6. Diameters shrinkage provided/reached in (a) PAA nanofibers; (b) PI nanofibers after the imidization process and (c) and (d) after the carbonization process, conducted at 1000°C for 1 h. Reprinted with the permission from (journal of physical chemistry B letters, 2007, 111, 11,350–11,353) copyright (2007) American Chemical Society.

Kim et al. investigate the correlation between the morphological properties of mats with the polymer concentration. Indeed, different electrospun polymeric solutions were prepared by dissolving 12, 14, 16 and 18 wt% of PVDF in a mixture, based on acetone and dimethylacetamide (DMAc, volume ratio of 7/3 weight). PVDF nanofibers are characterized by an average diameter close to several hundreds nanometers and a microporous structure, defined by the interconnections between all nanofibers. As confirmed theoretically, it is possible to observe that the diameter increases with the increasing of polymer concentration: higher is the polymeric concentration, higher are the diameter values.

In order to obtain highly porous carbon-based nanofiber mats, derived from PVDF nanofibers, Yang et al. [34] synthesized PVDF nanofibers, starting from a polymeric solution, containing PEO (0.06 g) and PVDF (1 g) dissolved in 9 g of mixture of DMF and deionized water (5:3 volume ratio). The addition of PEO together with water as non-solvent for PVDF guarantees the formation of microporous structure on PVDF nanofibers surface. The heating treatment, selected in order to convert the PVDF precursor into carbon, is based on two different steps, named dehydrofluorination and carbonization. Dehydrofluorination enhances the thermal stability of the material before the carbonization step. Different from the thermal stability conducted for PAN nanofibers, which is achieved at low temperature close to 300°C, for PVDF the stabilization

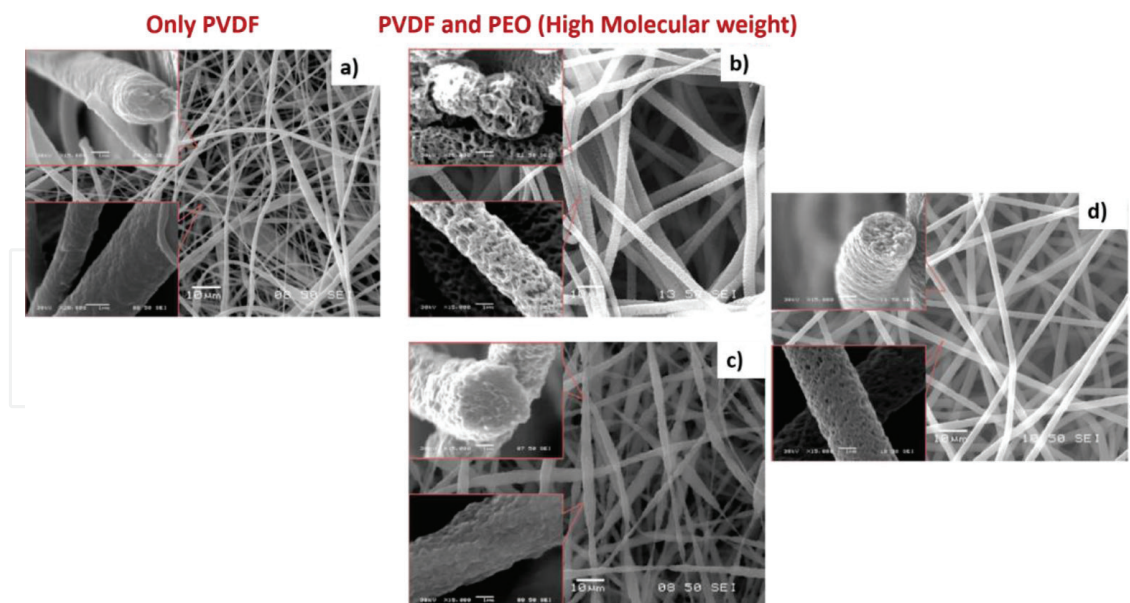


Figure 7. Modulation of porous structure in the PVDF nanofibers, obtained by adding PEO and increasing the relative humidity. (a) Only PVDF-based nanofibers; (b) PVDF and PEO nanofibers collected when the relative humidity is 45%; (c) relative humidity is 35%; (d) PVDF and PEO nanofibers obtained with a lower PEO concentration. Reprinted with the permission from (carbon, 2011, 49, 3395–3403) copyright (2011) Elsevier.

occurred through a heating treatment at 400°C in air. Since this temperature is much above the temperature of melting point (190°C), dehydrofluorination is commonly provided as chemical treatment at low temperature, introducing a large number of C–C bonds into the main chains. The PVDF nanofibers are soaked in the solution containing DMF and methanol (9:1 volume ratio) as solvent, and the chemical compound (DBU: 1,8-diazabicyclo[5.4.0]undec-7-ene) that is added for each unit of vinylidene fluoride unit. The carbonization process was carried out at temperature higher than 1000°C in N₂ flow for 1 h. The PEO concentration, the amount of water in the polymeric solution and the relative humidity reached when the nanofibers collected play a crucial role to control the porous morphology of the sample, as represented in **Figure 7**. When PEO is absent in the initial polymeric solution (**Figure 7a**), PVDF nanofibers show a certain surface roughness and few pores inside the mat. Whereas, high relative humidity combined with PEO provide the formation of pores on the nanofiber surface (**Figure 7b**). Both of the presence of water and PEO induce the pores distributions all through inside the fibers (**Figure 7b, c and d**); one pore is connected with each other. It is possible to define a correlation between the pores distributions (on the nanofibers surface and on the bulk) with PEO molecular weight and PEO concentration (**Figure 7d**). Indeed higher is the molecular weight of PEO, higher is no-solubility of PVDF, leading thus to increase the porous structure inside the mat and on nanofibers surface. The same trend can be observed when PEO concentration increases: the pores number on the surface is larger when PEO concentration increases.

Poly(vinyl alcohol) (PVA) is used to obtain carbon nanofibers, starting from named green polymeric solution, although its low carbonization yield and low decomposition temperature. PVA nanofibers, indeed, are obtained starting from a water-based solution and the carbonization process is implemented at low temperature, close to 500°C, for 3 h under flow of argon and hydrogen [35]. The main parameter, which influences the diameter distribution of

PVA nanofibers, is the pH of polymeric solution. At neutral pH value, the diameters are in the order of hundreds nanometers [36]; while the average diameters increase as the basic pH increases. On the contrary, when the pH becomes more acid a no continuous polymeric jet is guaranteed during the electrospinning process, inducing the formation of charged droplets

4. Carbon nanofibers morphology and composition

Considering PAN as the most suitable carbon precursor, it is possible to obtain different carbon nanofibers morphology, for example, core-shell nanofibers, hollow nanofibers, porous nanofibers, as summarized in **Table 1**.

4.1. Core-shell and hollow nanofibers

These kind of nanofibers is obtained by modifying the electrospinning setup into a coaxial electrospinning. Coaxial electrospinning is carried out by a concentric disposition of two syringe holders, where two spinning solutions can be loaded, as represented in **Figure 8**.

Core-shell nanofibers are made of a shell, typically natural or synthetic polymers, and by a core that can be a solvent or a polymer, known as sacrificial polymer. In this latter configuration, through a post-process, such as heating treatment and/or chemical treatment,

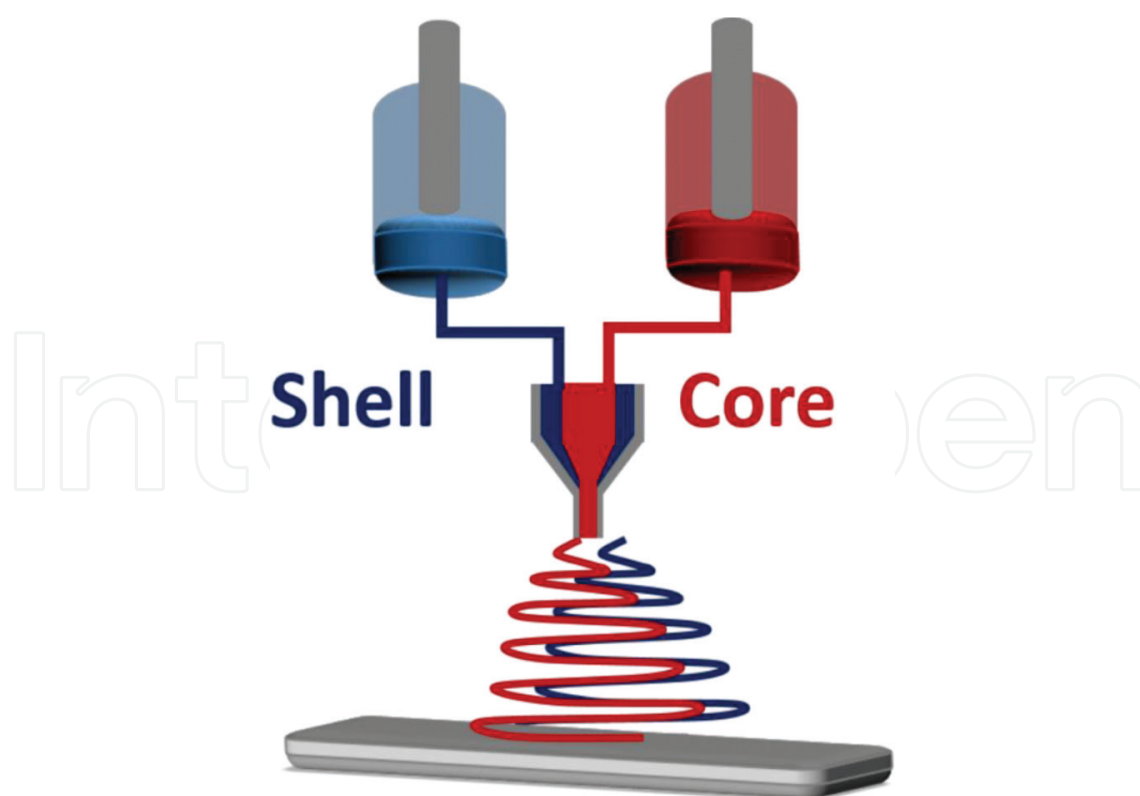


Figure 8. Sketch of coaxial electrospinning used in order to obtain core-shell nanofibers or hollow nanofibers.

the core was removed, leading thus to the formation of hollow nanofibers [37]. Therefore hollow nanofibers show an empty core and a shell, also defined wall, based on polymer, ceramic or carbon-based materials. Zussman et al. used coaxial electrospinning in order to obtain hollow carbon-based nanofibers. In this work, the shell solution contained 12 wt% of PAN dissolved in DMF, selected as carbon precursor; while the core is obtained starting from a solution of Poly(methyl) methacrylate (PMMA) mixed in a solvent of DMF/acetone. The acetone is no solvent for PAN, leading thus to create, during electrospinning process, a solid interface between shell and core and consequently a dried core-shell nanostructure. Core-shell nanofibers mat was thermally treated in order to ensure the carbonization of shell (PAN nanostructures) and simultaneously the completely degradation and decomposition of PMMA core. The heating treatment is achieved through two steps: the first step is in air at 250° to thermal stabilize the sample and the second step is in inert atmosphere (N₂ atmosphere) at 1100°C. These hollow nanofibers show an external diameter equal to 7 μm and an internal diameter close to 2 μm.

Another way, provided to obtain hollow nanofibers, is based on the preparation of electrospun solution similar to an emulsion mixture [38, 39]. Kim et al. [38] prepared the emulsion-like solution mixed two immiscible polymers: PAN as carbon source, forming the continuous phase of solution, and PMMA, which constitutes the dispersed phase. The collected nanofiber mats results to be a core-shell nanostructure: the shell is made of continuous and long fibers of PAN, whereas the core is discontinuous part of PMMA. The carbonization process ensures the formation of hollow carbon-based nanofibers through the completely degradation of PMMA polymers.

5. Application of carbon nanofibers for energy conversion

The great importance to identify new models to make human development sustainable for the environment has pushed and potentiated the scientific research in the area of renewable energy sources. Nanotechnologies are gaining a prominent role in driving this revolution toward sustainability. Indeed nanomaterials offer several advantages with respect to their macroscopic counterparts. First of all, since they offer high specific surface area combined to outstanding mechanical and electrical properties, they grant the design of high-performing devices [32, 33]. Among the different nanostructures that have been proposed in the area of EEC, nanofibers by electrospinning belong to one of the most versatile class of nanomaterials, able to be easily optimized with different morphologies and with a set of final properties that can be tuned as required by the final application [34, 35]. The development of carbon nanofibers, as electrodes in EEC devices, ensures great improvements of their overall performances [32–35]. In particular, all EEC devices described in this book chapter represent the most promising technologies in terms of renewable energy. In the last decades, the new renewable sources were developed in order to supply the 50% of energy demand, minimizing greenhouse gas emissions (GHG), limiting environmental pollution and producing power through electrochemical conversion of new fuels, such as wastes, CO₂ and other compounds.

5.1. Energy production

5.1.1. Fuel cells

Fuel cells represent an important class of electrochemical devices for energy conversion. They are capable of directly convert the chemical energy present in a wide range of molecules into electrical energy. The starting molecules, as hydrogen and methanol, act as fuel and, thanks to presence of the proper catalysts, oxidation reactions occur at the anode of the systems, resulting in the production of electricity [1]. Actually different fuel cell technologies have been developed, that make possible to use as starting fuels not only small size molecules as hydrogen, methanol and ethanol, but also more complex solid organic matter present in different kind of wastewaters and soils as in happen in microbial fuel cells (MFCs) [39]. The use of carbon-based nanofibers is quite frequent in this area, since they combine good electrochemical stability with high electrical conductivity, while offering several strategies for their decoration and coupling with the required catalysts. In microbial fuel cell, particular class of microorganisms, named exoelectrogenic, catalyzes the oxidation reaction, which permits the conversion of chemical energy of organic matter of wastewater into electricity. These kinds of bacteria are able to directly release electrons that can be accepted by the anode of the device, during their metabolic activity. The electrode plays a role similar to that of different minerals that exoelectrogenic bacteria can find in their natural environments, for example, freshwater and seawater sediments [40]. Carbon-based nanomaterials are intriguing materials for the fabrication of anodes for MFCs, since they offer good electrochemical behavior and optimal morphological features that can favor bacteria growth on them [41].

An interesting possibility to improve the performances of FCs is the use of oxygen at the cathode of the system as the final electron acceptor. The reaction that occurs in these reactors is the so-called oxygen reduction reaction (ORR). The complete ORR is proposed in Eq. (2), it permits to use 4 electrons for each molecule of reacting oxygen.



Actually to promote the ORR reaction according to the pathway described by Eq. (2), avoiding the formation of dangerous and unwanted side products as H_2O_2 , the presence of a proper catalyst is mandatory. The most important catalyst for this reaction is Pt, which is a rare and expensive metal [42]. Many efforts are spent worldwide to identify and optimize substitutes for Pt-based catalysts, able to offer the same catalytic efficiency but with a significant cost reduction.

Carbon-based nanofibers by electrospinning offer an interesting opportunity to design high-performing cathodes. Indeed selecting the proper precursors for the fabrication of nanofiber it is possible to add spontaneous doping sites made of heteroatoms that have demonstrated to be quite active toward the ORR. In paragraph 3.1 PAN has been introduced as the reference precursor for the synthesis of carbon-based nanofibers, due to its high carbon yield during the pyrolysis process. The structure of the polymer chain of PAN was proposed in **Figure 5**, showing the presence of $-\text{C}\equiv\text{N}$ groups along the chain. Properly controlling the thermal treatment, it is possible to fabricate nanofibers with a good degree of graphitization in which several N-based defects can be present into the graphitic structure of carbon, as proposed in

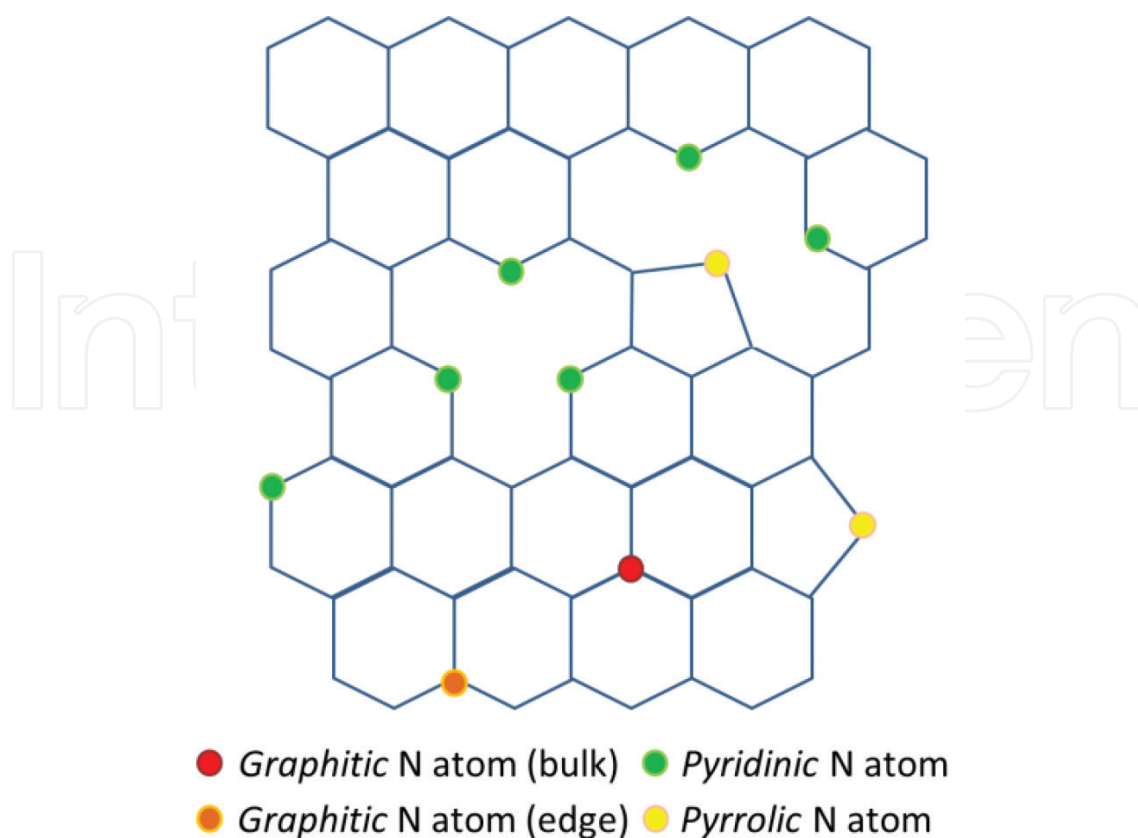


Figure 9. Sketch of a graphitic plane with the different nitrogen defects that can be formed during the pyrolysis process starting from PAN precursor.

Figure 9. It has been reported by several works in the literature that those defects actually behave as N-doping sites for the carbon nanofibers, and their presence can be controlled during the fabrication process [43]. The N-based defects in the graphitic structure of the nanofibers play an important role as active catalytic sites toward the ORR. Moreover several strategies are possible to decorate the carbon-based nanofibers with metal-based catalyst, with the possibility to optimize a co-catalysis process.

5.1.2. DSSC

Photovoltaic devices whose working principle involves electrochemical reactions have been proposed, they are the dye-sensitized solar cells (DSSCs). As in traditional solar cells, photons are directly converted in electrons, but in DSSCs organic molecules, that is, the dye, are responsible for the adsorption/conversion processes [36, 37]. A wide band gap semiconductor, which is usually TiO_2 , captures the produced electrons and the regeneration of the dye is granted by the presence of a redox mediator into the electrolyte. The most frequently used redox couple is iodide/triiodide (I^-/I_3^-), that is then reduced at the counter electrode (CE). The design of the CE is particularly challenging, since it must show high chemical resistance to the aggressive redox couple used in DSSC and preserve high efficiency over time in catalyzing the triiodide reduction. Platinum is the reference catalyst employed at the CE in DSSC, but high is the interest to substitute it with high-performing materials, leading thus to keep

low the cost of the final devices and overcome the issues related to Pt that rapidly degrades because of the exposure to iodide/triiodide. The use of carbon-based nanofibers in this area has been especially important for the optimization of new counter electrodes [44, 45]. High efficiency of DSSC are strictly related to the proper design of photo-anodes, especially related to the different interfaces among all materials, that is, dye/semiconductor/electrode. Indeed the optimization of charge injection after their photo-generation is a key step to avoid charge recombination. Electrospinning offers interesting possibilities to optimize these interfaces by the preparation of composite nanofibers. An interesting example is the work by Hieu et al. [46], in which the authors optimize a photo-anode made of core/shell nanofibers with a core made of highly graphitized carbon and TiO_2 as the outer shell. The nanofibers were obtained with a starting solution made of PAN as the carbon precursor and titanium isopropoxide added to polyvinylpyrrolidone (PVP) as the TiO_2 source. The resulting DSSC performed extremely well, reaching an efficiency of 7.5%.

5.2. Energy storage

5.2.1. Lithium ion batteries

Lithium ion batteries (LIBs) are a key technology for energy storage. A LIB is made of negative and positive electrodes that can both intercalate Li^+ ions reversibly. The electrodes are separated by conducting non-aqueous electrolyte containing lithium ions. Discharge correspond to use of the battery, during this phase Li^+ ions grant the current flow from the negative to the positive electrode. The reverse operation, called charge, requires the use of an external voltage. Under the external potential, lithium ions are forced to move from the positive electrode to the negative one. At the negative electrode, lithium ions are trapped into the porous material forming the electrode during a process named intercalation [47]. Good examples, which show the use of nanofibers by electrospinning in LIBs, are especially related to the preparation of anodes, where the intercalation process causes huge mechanical stress to the materials, usually limiting their durability. The possibility to decorate electrospun carbon-based nanofibers with metal oxides is an intriguing strategy to reduce the size of the metal oxide down to the nanoscale, significantly improving the mechanical robustness of the material. The synthesis proposed by L. Ji et al. [48], is relatively easy. The authors obtained the starting polymer solution based on the addition of the oxide precursor into the solution already containing the carbon precursor. They synthesized carbon nanofibers decorated with $\alpha\text{-Fe}_2\text{O}_3$ nanoparticles, demonstrating homogenous dispersion of the nanoparticles along the carbon-based nanofibers. The thermal process is carefully optimized in order to proper control the carbonization of the nanofibers, and at the same time favor the nucleation of the semi-conducting oxide nanoparticles. The resulting nanofibrous composite anode showed good performances, especially in terms of its reversibility. Another interesting oxide used in LIBs anodes is SnO_x . Unfortunately, despite the huge potential of this material, the problem of its stability over time, due to the effect of the intercalation process, make impossible its real use. New approaches and processes are investigated to reduce the effect of the volume variation caused by Li ions intercalation. The fabrication of nanostructures usually helps to alleviate the problem of volume variation. Zhu et al. [49] demonstrated the possibility to co-synthesized SnO_x nanoparticles directly on 1D carbon-based nanofibers, through several phases: (i) an

electrospinning step, (ii) a calcination process. The resulting anodes showed extraordinary good cycling durability. The development on smart systems and new portable electronic tools has required the development of devices for energy storage able to couple light-weight to small dimensions and frequently to high mechanical flexibility. Carbon-based nanofibers represent a unique opportunity for electrochemical energy storage for the design and optimization of flexible systems. It is indeed quite interesting to consider that carbon-based nanofiber mats obtained by electrospinning usually preserve high flexibility and bending ability after the pyrolysis treatment. So that processing the nanofiber mat in such a way to have it as a freestanding membrane, it is possible to fabricate incredibly flexible electrodes that can be integrated in LIBs. As an example the work of Samul et al. [50] can be considered. They demonstrated that carbon-based nanofibers were able to preserve their high flexibility even if decorated by MnO nanoparticles for the fabrication of high-performing anodes for flexible LIBs.

5.2.2. Supercapacitors

Supercapacitors (SCs) are able to store impressively higher energy density than traditional capacitors, thanks to the creation of an electric double layer (EDL) as the key mechanism to store the charges. Moreover, SCs are able to accept and deliver charges quite faster than batteries and with a quite higher durability to charge/discharge cycles than batteries. Due to these features, SCs are usually considered as the technology filling the gap between conventional capacitors and LIBs [51]. The use of carbon-based nanofibers to design electrodes for supercapacitors is strictly related to high interest to develop flexible, portable and easy-to-integrate SCs for smart electronics. As already introduced discussing flexible LIBs, carbon-based nanofibers combine unique mix of electrical conductivity, mechanical flexibility and electrochemical stability that make a great material to design flexible systems. These impressive properties are coupled to the high versatility offered by the electrospinning technique that makes relatively easy to prepare composite and decorated carbon nanofibers [52].

5.3. Fuels

Hydrogen is progressively gaining importance as one of the possible green fuels of the future, able to become a potential substitute for fossil fuels. The electrocatalysis of the hydrogen evolution reaction (HER) is the critical step for this technology, pushing intense research to identify high-performing and low-cost catalysts. The availability of catalyst, able to efficiently drive the HER, while keeping the overall costs of the process, is indeed the mandatory requirement for large-scale H₂ production by this technology. In the area of electrochemical water splitting, carbon-based nanofibers by electrospinning are frequently used as a conductive and robust matrix to offer a support for other catalysts. Recently the huge potential of composite carbon nanofibers has been considered in this area too. Zhao et al. synthesized N-doped carbon nanofibers with embedded Co nanoparticles. They demonstrated the superior electrocatalytic performance of the resulting electrode, explaining the results as due to the ability of the material to expose two catalytic sites, the nitrogen defects into the main carbon nanofibers and the Co nanoparticles [53]. Again with the aim to identify possible substitute to expensive noble metal-based catalysts, Chen et al. optimized an interesting method to directly synthesize WO₃-x in carbon-based nanofibers. They improve the thermal treatment

to induce graphitization of the starting electrospun nanofibers, as well as the synthesis of the oxygen vacancy-rich WO_{3-x} [54]. In recent years a new interest emerged in developing efficient electrochemical processes for the conversion of the environmental harmful CO_2 into new high-value products. Efficient catalysts are needed to grant good conversion efficiency, possibly involving low-cost materials that can help making competitive the process. In this area carbon-based nanofibers obtained by the pyrolysis of PAN nanofibers have been successfully investigate as catalysts of CO_2 reduction into CO. Kumar et al. demonstrated that nitrogen defects play a crucial role in catalyzing the reaction, with a mechanism quite similar to the one demonstrated for the catalysis of the ORR by the same class of materials [55].

6. Summary

The ever-increasing energy demand, related to the progress of human activities, favored an intense scientific research for the development of new technologies able to harness, convert and store environmental energy with safer and more efficient approaches than the traditional ones. In this frame, electrochemical processes for energy conversion have emerged as a unique, versatile and reliable platform to design efficient energy systems. This chapter has shown the key advancements obtained in the area of EEC by the introduction of the electrospinning process to design a new generation of carbon-based electrodes starting from nonwoven nanofiber mats. Relevant examples of electrodes made of carbon-based nanofibers have been demonstrated in all the key EEC technologies, from photovoltaics to batteries, from fuel cells to supercapacitors, clearly showing the most promising strategies introduced up to now.

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