Abstract

Fiber-shape supercapacitors -also called wire-shaped supercapacitors WSSC-, represent one of the leading strategies for the development of energy storage devices that can be highly integrated into flexible systems. Unlike battery systems, supercapacitive storage mechanisms are particularly suitable for the development of wire-shaped devices because they feature less layered materials for the electrodes and often - as in the case of carbon-based electrodes - a single material that acts as both active material and collector. This makes it possible to develop devices with thicknesses below 1 mm, which is an important requirement for their integration into fabrics via industrial looms.

The power and energy densities of these devices are comparable to those of micro-supercapacitors, due to the short diffusion path of the ions [1]. At the same time, the geometry of the wire has a high predisposition to scalability, which is also included and studied directly in the literature [2][3][4]. Furthermore, research in this sector allows the study and development of innovative materials, which combine electrochemical properties with high mechanical properties.

In this dissertation, innovative technologies and materials are investigated to develop WSSCs. It aim to provide promising alternatives in the field of devices that can be integrated into technical fabrics and clothing for the purpose of powering portable devices and/or isolated sensors. For this reason, all scientific developments have been carried out with careful consideration of the constraints imposed by the scalability and integrability required for the industrial production and application.

The first investigation focuses on evaluating Carbon nanotube yarns (CNTy) as a starting material for the fabrication of wire-shaped electrodes suitable for WSSC applications. CNTy are composed entirely of aligned and spun single-walled carbon nanotubes, and exhibits a highly ordered graphene network unlike conventional carbon-based fiber obtained through the reduction of oxidized carbon structures. It

is therefore easy to activate its surface with chemical processes while preserving the inner networks and their conductive properties. Pristine CNTys shows an electrical double layer capacitance of 3 mF/cm in aqueous electrolyte 0.5M H_2SO_4 and they can reach, after electrochemical functionalization, a capacitance of 9.5 mF/cm with a cathodic gain of +450% (from 1.8 mF/cm to 10 mF/cm). The functionalized CNTy were analyzed and compared with pristine CNTy with x-ray photoelectron spectroscopy (XPS), Raman spectroscopy and observed at Field emission Scanning Electron Microscopy (FESEM).

A significant part of this thesis focuses on the development and characterization of polymer-based electrolytes and separators compatible with CNTy electrodes. Porous electrolytes and separators have been studied from their synthesis, obtained with very different methods - cross-linked polymer matrices, electrodepositions, non solvent induced phase separations, solvent casting - using a large variety of polymers - Polyethylene glycol PEG and polypropylene glycol PPG acrylates oligomer, copolymers based on Polyacrylonitrile and Polyvinylidene fluoride - coupled with lithium salt and ionic liquids with large potential windows in order to maximize the energy density. The aim was to improve ionic conductivity and reduce device internal resistance, without compromising the mechanical properties required for integration. The final products -that, at room temperature, show conductivity between 10^{-4} mS/cm (PEG-based electrolyte, PVDF porosus separator soaked by ionic liquid) and 10^{-3} mS/cm (PAN-based solid electrolyte)- have been characterized in detail with techniques, including IR spectroscopy, Impedance spectroscopy, Viscosimetry. Finally, devices have been assembled with each electrolyte and properly characterized, yielding maximum energy densities on the order of 10^{-6} Wh/cm, and corresponding power densities ranging from 10^{-8} W/cm to 10^{-4} W/cm depending on the electrolyte used.

In order to employ CNT yarns as effective electrodes, it was also necessary to reduce the ohmic drop occurring at the interface between the carbon-based material and the external metallic current collectors. For this purpose, a two-step electrodeposition technique was developed, consisting of an initial deposition in an organic electrolyte, followed by a second step in an aqueous medium. This process enabled the formation of a thin metallic copper layer on the hydrophobic CNTy surface. The deposited copper exhibited good electrical interface with the CNTy and was compatible with standard soldering techniques, effectively providing a low-resistance electrical junction. Moreover, a reduction in resistivity was observed, from (12.8 $\pm$ 0.7) Ω/m to (3.64 $\pm$ 0.2)Ω/m.

From an engineering point of view, assembly strategies for the devices and three-electrode cells have been implemented and described in order to improve the reliability and repeatability of the electrochemical measurements. This is mainly due to two factors: i) working with CNTy and wire-shaped devices represents a challenge in finding assembly strategies for the devices and three-electrode cells due to absence of commercial setups studied for this geometry, and ii) the need to apply the scientific solutions found to an industrial context. In this last case the design of the devices has foreseen their assembly and integration with the machinery already available in the factory representing a reduction of costs. Combining the scientific results of this work with a realistic and utilitarian approach.

To summarize, this research aims to contribute to the advancement of WSSCs technology using innovative materials -including polymers, carbon nanotube yarns (CNTy), and ionic liquids- and adapting well-estabilished techniques -such as electrodeposition and non-solvent induced phase separation (NIPS)- to this field of research. The resulting devices are flexible, thin, and suitable for integration into wearable systems. Moreover, the methodologies presented herein can be applied to a wide range of materials and geometries with the potential to yield more performing, cost-effective and eco-friendly WSSCs.