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Flexible, ionic liquid-based micro-supercapacitor produced by supersonic cluster beam deposition

L.G. Bettini [a], P. Piseri [a], F. De Giorgio [b], C. Arbizzani [b,1], P. Milani [a], F. Soavi [b,1,*]

[a] CIMaINa and Physics Department, Università degli Studi di Milano,Via Celoria 16, 20133 Milano, Italy
[b] Department of Chemistry "Giacomo Ciamician", Alma Mater Studiorum – Università degli Studi di Bologna, Via Selmi 2, 40126 Bologna, Italy

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ABSTRACT

Power generation and storage in electronics require flexible, thin micro-electrochemical energy storage/conversion systems. Micro-supercapacitors (μSCs) with double-layer capacitance carbon electrodes are attracting much attention for their capability of delivering short power pulses with high stability over repeated charge/discharge cycling. Supersonic Cluster Beam Deposition (SCBD) is an effective strategy for the development of nanostructured, binder-free porous carbon electrodes on temperature sensitive substrates including polymers. We exploited SCBD for the development of a flexible, planar μSC featuring nanostructured carbon (ns-C) electrodes deposited on a plastic Mylar substrate and N-trimethyl-N-propyl-ammonium bis(trifluoromethanesulfonyl) imide (N_{1113}TFSI) ionic liquid electrolyte. The electrochemical performance at different temperatures of the μSC which operates at 3 V above RT up to 80 °C with a capacitance density approaching 10 F cm^{-3} and delivering maximum specific energy and power densities of 10 mWh cm^{-3} and 8-10 W cm^{-3} with long cycling stability over 2×10^4 cycles is here reported and discussed.

1. Introduction

The recent boom in multifunction, light and flexible portable electronic equipment, the increasing need of low-energy cost and autonomy for wireless sensor networks for smart environments and biomedical applications, and for ancillaries in automotive, e-cards and smart packaging has raised the problem of developing sufficiently compact and/or flexible, multifunctional electronic components. Self-powered and self-sustaining integrated systems require electrochemical energy storage/conversion devices like rechargeable micro-batteries and micro-supercapacitors (μSCs) that should be miniaturized down to flexible smart card size (<1 mm thick) by low cost and eco-friendly strategies. Compared to micro-batteries, μSCs with high surface area carbon electrodes store energy by electrostatic process. While μSCs feature much lower energy density than batteries, they show faster time response and superior cycling stability, which are of paramount importance for applications, like sensors, where repeated power peaks are required. Furthermore, carbonaceous electrodes of supercapacitors can be easily processed for in-plane, flexible architectures and being free of precious, rare or toxic metals like Co and Ni, hold much promise for a green and sustainable energy harvesting scenario due to the low cost of raw materials and their recyclability [1–6].

Toward the on-chip integration of μSCs, it is pivotal to replace the traditional prismatic design with an in-plane architecture. Several strategies that include novel electrolyte formulations and electrode preparation procedures by planar microfabrication techniques are under investigation [7–10]. One important challenge in thin, flexible μSC development is how to immobilize the electrolyte. Ionic liquids (ILs), for their unique properties of low volatility, high chemical, thermal and electrochemical stability and good conductivity in wide temperature ranges, even in combination with polymer matrixes or as gels may represent a strategy to improve system life [11–17]. IL-based electrolytes have been demonstrated to increase the supercapacitor energy delivered at high voltages and power rates both of large size and micro-systems. It has also been recently demonstrated that supercapacitors working with ILs feature leakage currents and self-discharge that are lower and less affected by the temperature than those of the cells with conventional electrolyte [17]. The high

* Corresponding author. Tel.: +39 051 2099797; fax: +39 051 2099365.
E-mail address: francesca.soavi@unibo.it (F. Soavi).
[1] ISE member

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boiling point of ILs also is an unique advantage for the development of thin electrochemical devices capable to operate above room temperature (RT).

Several carbonaceous electrode materials have been already investigated for μSC, including CNTs, activated carbon, onion carbons and graphene with the aim of increasing the volumetric capacitance [8–10]. Although these materials have been successfully used for the production of flexible μSC [18–24], significant research efforts are currently devoted to the development of efficient and reliable methods for the fabrication of flexible carbon based electrodes.

Deposition of nanostructured carbon (ns-C) by Supersonic Cluster Beam Deposition (SCBD) has been recently demonstrated to be a very promising strategy for the development of porous carbon thin film electrodes featuring high capacitance density in ionic liquid electrolytes [16]. This technique presents intrinsic advantages, such as the avoidance of binders, the compatibility with temperature sensitive substrates and standard planar microtechnology processes that are strict requirements for the development of a high throughput microfabrication technique for the fabrication of planar and flexible μSC.

SCBD consists in the room temperature deposition under high vacuum conditions of nanoparticles accelerated in a free jet expansion to form a beam in the molecular regime [25]. Characterized by low kinetic energy at impact (upon particle deposition), it produces a random stacking of nanoparticles leading to nanostructured materials with a porosity that extends over different scales: from the pristine clusters morphology as determined by gas-phase aggregation, to the grains distribution throughout the surface as determined by the deposition process. Ns-C deposited by SCBD consists in a high surface area disordered carbon characterized by substantial dominance of sp^2 hybridization [26]. This results in a very low-density (ca. 0.5 g cm^{-3} [27]) and high specific surface area (ca. 700 $m^2 g^{-1}$ [28]) which have been shown to be beneficial for electrochemical energy storage applications [16,29,30].

Here, we exploit SCBD to develop a flexible and plastic, carbon-based planar μSC which can operate at 3 V up to 80 °C in a flat and bent configuration. The proof of concept is demonstrated by an μSC with N-trimethyl-N-propyl-ammonium bis(trifluoromethanesulfonyl) imide (N_{1113}TFSI) IL electrolyte. The electrochemical performance at different temperatures of the μSC is reported and discussed.

2. Experimental

2.1. μSC fabrication

Fig. 1 reports the schematic picture of the flexible, IL-based μSC. Two ns-C electrodes of 1 cm^2 area each and thickness of 320 nm or 500 nm, separated by a 2 mm gap, were deposited by SCBD over a Mylar substrate (20 μm thickness) previously coated by a thin metallic film (platinum with ca. 200 nm thickness) as current collector. Such simple μSC design aims to be considered as a benchmark for further optimization (in terms of electrode geometric area and size, electrode spacing and current collector material). Hereafter, the labels μSC-320 and μSC-500 indicate the supercapacitors with ns-C layers of 320 nm and 500 nm, respectively.

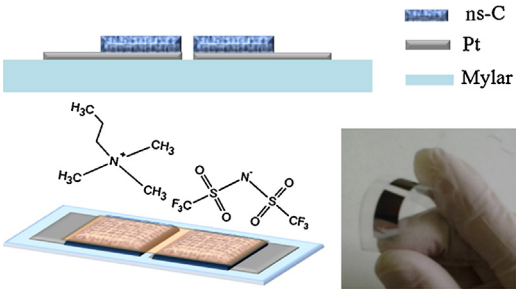

Fig. 1. Schematic picture of the flexible, IL-based μSC fabricated by SCBD.

Platinum deposition is carried out by Ar ion sputtering of a Pt target under vacuum (with an RF magnetron ion beam source; working pressure ~10^{-4} mbar). The carbon clusters deposited on the top of the Pt coated Mylar are produced in a Pulsed Microplasma Cluster Source (PMCS) by the ablation of a graphite target [31]. The mixture of clusters and inert gas leaves then the PMCS internal cavity by expanding through a nozzle, thus forming a seeded supersonic beam of aerodynamically accelerated nanoparticles that are finally collected on the substrate located on the beam trajectory to form a cluster-assembled carbon film. As the cluster kinetic energy is low enough to avoid fragmentation upon landing, a nanostructured film of relatively soft-landing particles retaining the structural properties of the gas-phase aggregates is grown. A substantial advantage or SCBD compared to traditional physical vapor deposition methods is its compatibility with thermolabile polymeric substrates, thus allowing the possibility of depositing nanostructured films on flexible and stretchable substrates [26].

The as-deposited ns-C electrodes were, then, coated by a fiber glass separator (Whatman,GF/F, dried before use) soaked with the N_{1113}TFSI (99.5%, Solvionic, used as received) IL. At RT, the IL features an electrochemical stability window of 5.7 V and a conductivity of 9.3 mS cm^{-1} [15]. A silver foil and an activated carbon fabric (Spectracorp 2225, 2500 m^2/g) were vertically stacked with the μSC electrodes and separated from them by the separator and used as quasi-reference electrode and counter electrode, respectively, for the electrochemical tests in 3-electrode mode. The area exposed to the electrolyte of the silver foil and the activated carbon fabric was ca. 0.5 × 0.6 cm^2. The μSCs were assembled in dry box (MBraun, Atmosphere, H_2O and O_2 <1 ppm).

2.2. μSC characterization

The cyclic voltammetries (CV) and galvanostatic charge/discharges (GLV) were performed using BioLogic VSP and VMP multichannel potentiostat/galvanostats at 30 °C, 60 °C and 80 °C (ICT5, 4 FALC mini incubator, FALC Thermoblock). μSC-320 and μSC-500 were tested outside (between glass slides in the case of the flat configuration sealed with Kapton tape) and inside the dry box, respectively. The volumetric densities of capacitance, energy and power were calculated by considering electrode volumes of 3.2×10^{-5} cm^3 or 5×10^{-5} cm^3 and μSC volume of 6.4×10^{-5} cm^3 or 1×10^{-4} cm^3 which only take into account the area and the thickness of the two carbon electrodes. The areal densities refer to the area of one electrode (1 cm^2). The electrochemical tests were carried out both with flat and bent μSCs. In the latter case the μSC was wrapped on a glass tube of 2.2 cm diameter.

3. Results and discussion

A CV survey was performed at first in a 3-electrode, flat configuration and at room temperature (RT) for the evaluation of the capacitive response of the μSC-500 electrodes at different scan rates, and the results are shown in Fig. 2. Fig. 2a shows the results at 20 mV s^{-1}. The electrochemical stability window (ESW) of N_{113}TFSI electrolyte at the μSC electrode is ca. −2/1.5 V vs Ag and 3.5 V wide. After the first anodic sweep, that reveals an irreversible oxidation process presumably promoted by the presence of chemisorbed oxygen on the surface of ns-C [27], the