Cluster-assembled Carbon Thin Films and Nanocomposites for Electrochemical Energy Storage

L.G. Bettini[*,§], P. Milani[*] and P. Piseri[*]

[*]CIMaINa and Physics Department, University of Milano, Via Celoria 16, 20133 Milano, Italy
[§]lucagiacomo.bettini@unimi.it

ABSTRACT

Supercapacitors are extremely versatile energy storage devices that store energy by the electrostatic separation of charged species at the interface between a solid electrode and an electrolyte forming the so called electric double layer (EDL). Although the supercapacitor market is rapidly growing, the continuous claim to improved energy and power storage pushes a lot of efforts to the synthesis of carbon based materials with tailored properties. Moreover, powering mobile/personal small-scale devices with on-chip integrated micro-supercapacitors is still a challenge that can only be addressed by the development of a scalable technique for the deposition and patterning of highly porous carbons in the form of thin films. Here the deposition of nanostructured carbon (ns-C) thin films and nanocomposites by Supersonic Cluster Beam Deposition (SCBD) is reported to be a viable route toward the fabrication of miniaturized and/or integrated electrochemical energy storage devices.

Keywords: carbon, supercapacitors, nanostructured thin films, gas-phase deposition, supersonic cluster beam deposition

1 INTRODUCTION

The rapid growth of mobile/personal electronics for applications in sensors, communication, health care, and environmental monitoring is pushing the demand for the sustainable and independent operation of small-scale systems. Currently, the powering of these devices still relies on batteries. The amount of batteries required increases in proportion with the increase in the number of mobile electronic devices used resulting in challenges for recycling and replacement of the batteries as well as concerns about potential environmental pollution [1]. Scientific efforts to develop sustainable, efficient, miniaturized, planar and integrable on-chip energy-storage systems are dramatically needed [2]. Power generation and storage for microelectromechanical systems (MEMS), miniaturized biomedical devices, sensors and integrated on-chip components, can significantly benefit from the fabrication and integration of planar thin film supercapacitors [2].

However, porous carbon fabrication protocols commonly employed in the manufacturing of supercapacitors are not easily integrable with thin film deposition processes and/or micro-patterning techniques. Although the amount of works in literature reporting on novel techniques for the synthesis of planar thin film carbon supercapacitors is rapidly increasing [2-5] for an effective miniaturization and planarization of supercapacitors it is essential to develop the ability of synthetize and deposit nanostructured porous materials in an efficient and reliable way that allow a fine control over the shape, thickness, morphology and structure of the carbon electrodes, possibly avoiding expensive and/or complicated fabrication steps such as photolithographic techniques, high-temperature processing and aggressive chemical treatments.

The deposition of carbon nanoparticles with low kinetic energy by Supersonic Cluster Beam Deposition (SCBD) is an effective bottom-up approach to the room temperature production and integration of nanostructured films on any substrate which is vacuum-compatible, allowing semi-continuous manufacturing in clean high-vacuum conditions.

2 SUPERSONIC CLUSTER BEAM DEPOSITION

The fabrication of complex devices by integrating of gas-phase nanoparticles with planar microtechnologies requires a very high degree of control on the lateral resolution of the nanoparticle deposition process, mild processing conditions (avoiding high temperature and aggressive chemicals), low contamination. In order to be industrially competitive the process must be compatible with standard top-down planar microfabrication technologies, highly scalable and low-cost.

Supersonic Cluster Beam Deposition (SCBD) fulfills these requirements: it consists in the deposition under standard high vacuum conditions (used for PVD coatings) of neutral nanoparticles (few nanometers in diameter) accelerated in a free jet expansion to form a supersonic seeded beam [6, 7]. The kinetic energy acquired by the nanoparticles is of the order of fraction of ev/atom thus preventing fragmentation of the nanoparticles upon landing

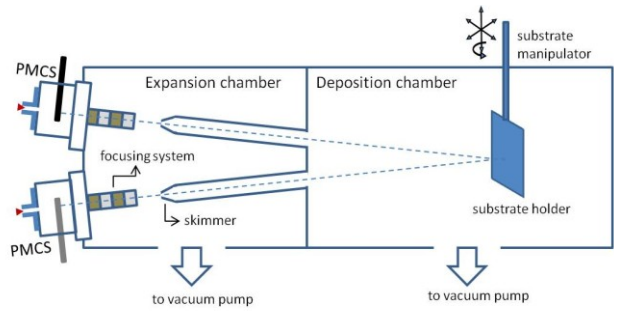

Figure 1: Sketch of a Supersonic Cluster Beam (SCBD) apparatus equipped with two Pulsed Microplasma Cluster Sources (PMCS)

on the substrate, while assuring good cohesion and adhesion. This results in a random stacking of nanoparticles leading to nanostructured films with very low-density and high porosity [6]. Due to the relatively low kinetic energy no substantial substrate heating is produced thus allowing the use of any kind of substrate, including the polymeric ones [8]. The use of supersonic expansions for cluster deposition allows to obtain very high deposition rates and highly collimated beam (divergence <20 mrad) which are suitable for the deposition of patterned nanostructured films by using stencil masks on substrates kept at room temperature. The resulting material is characterized by a low density compared to that of films assembled by depositing particles at high energies and it shows different degrees of order, depending on the scale of observation. The characteristic length scales are determined by cluster dimensions and by their degree of fragmentation and coalescence after deposition. The low degree of coalescence of clusters does not favor the formation of a hard material, however, it causes a large porosity and surface corrugation which can be beneficial for electrochemical applications [9, 10].

The coupling of the SCBD apparatus with a Pulsed Microplasma Cluster Source (PMCS) [11] and the application of aerodynamic separation concepts and techniques [12] to supersonic cluster beams for the purpose of nano-particle filtering, and for the production of high intensity particle beams allows to produce stable and intense nano-particle beams from most metallic elements and assures lateral resolution, deposition conditions, cleanliness and high throughput required by standard microfabrication technologies [6]. Furthermore, by rotating and rastering the substrate in the plane perpendicular to the nanoparticle beam it is virtually possible to coat samples of any large size area and geometry (from flat to complex curved surfaces).

Recently the feasibility of the Supersonic Cluster Beam Deposition (SCBD) technique for the deposition of nanostructured carbon (ns-C) thin films with promising electrochemical capacitive properties has been reported [10, 13].

Moreover, SCBD technique easily allow the synthesis of porous nanocomposite thin films by the mixing of clusters of different materials separately produced in distinct cluster sources (see Figure 1). In this way the two different materials do not interact during the cluster formation process and are mixed after the supersonic expansion, at the deposition stage. The low kinetic energy of the cluster in the beam avoids substantial fragmentation and coalescence upon clusters landing on the substrate and the result is a uniform mixing of the clusters. This strategy represents a powerful way to synthesize a virtually infinite range of porous nanocomposites with controllable and reproducible tuning of properties and composition. The embedding of nanoparticles in the carbon matrix can significantly affect ns-C properties such as porosity, density, surface area and material structure leading to improved physico-chemical properties.

3 PLANAR THIN FILM CARBON-BASED SUPERCAPACITOR FABRICATED BY SCBD

The supersonic cluster beam deposition (SCBD) of carbon clusters produced in a Pulsed Microplasma Cluster Source (PMCS) is a versatile technique for the fabrication of nanostructured carbon (ns-C) thin films with high porosity.

Ns-C deposited by SCBD consists in a high surface area disordered carbon characterized by substantial dominance of sp2 hybridization [9]. This material presents a typical density of ca. 0.5 g cm^{-3} [10] and a specific surface area measured by BET analysis of ca. 700 m^2 g^{-1} [9]. When ns-C is employed as active material in carbon-based capacitive electrodes this structure has been shown to originate an electric double layer gravimetric capacitance above 75 F g^{-1} both in aqueous [10] and ionic liquid electrolyte [13] .

These electrochemical performances, together with the relatively simple ns-C fabrication method, its compatibility with planar microfabrication technologies and the high control over the deposited material properties (e.g. thickness, surface roughness and porosity) obtained by the tuning of the deposition parameters empower the nanostructured carbon deposited by SCBD as an interesting material in electrochemical energy storage applications especially where extremely thin films of material are requested or where fragile substrates (e.g. polymers) are needed. The synthesis of porous carbon via SCBD presents several advantages, such as the compatibility with temperature sensitive substrates and with standard planar microtechnology processes, that may be pivotal toward the development of miniaturized thin film supercapacitors. The avoidance of binders to hold the ns-C to the current collector is another advantage of technological relevance toward the integration of nanostructured carbon electrodes on almost any kind of substrate (e.g. glass, silicon, paper

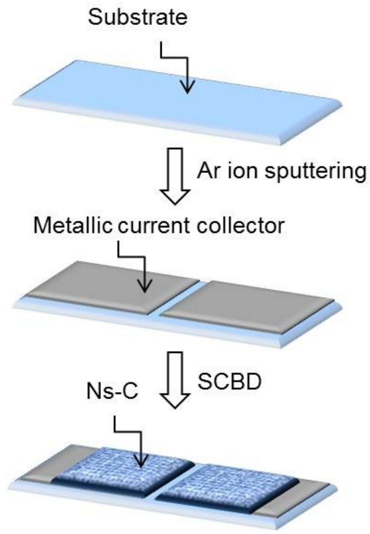

Figure 2: Sketch of the SCBD fabrication process of the planar ns-C based supercapacitors as reported in [13, 14].

and polymers). Moreover, the SCBD fabrication method allows to go beyond the traditional prismatic design of supercapacitors by replacing it with a 2D in-plane architecture that is pivotal toward their on-chip integration.

Supersonic Cluster Beam Deposition technique has been succesfully used for the room temperature fabrication of the proof of concept of planar thin film supercapacitors based on cluster assembled carbon (ns-C) and ionic liquids on both glass and flexible mylar substrates [13, 14]. The supercapacitors consisted of two in-plane ns-C electrodes with an area of ca. 1 cm^2 and thickness in the range between 200 and 500 nm separated by a non conductive gap of ca. 0.5 mm (Figure 2). A stencil mask was used during the SCBD process to obtain the desired electrode geometry. These devices showed an operating potential of 3 V 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 more than 10^4 cycles even at temperatures up to 350 K [14].

Although the measured performances in terms of energy and power density, together with the intrinsic versatility of SCBD, are appealing for the fabrication of thin electrodes for microscale energy storage devices, the use of ns-C produced via SCBD in practical applications requires a further development of material physico-chemical properties (e.g. nanostructure and electric conductivity).

The codeposition of nickel and carbon clusters by a SCBD apparatus equipped with two separate PMCSs (see Figure 1) has been reported to be a feasible route to deposit porous nanocomposites with improved electrochemical properties [15]. The presence of embedded Ni nanoparticles in the carbon film preserves the high specific surface area of ns-C and drastically improves its electrical conductivity. The electric double layer capacitance of Ni:C films featuring the same thickness (200 nm) and different nickel volumetric concentrations (0÷35%) has been investigated by electrochemical impedance spectroscopy employing an aqueous solution of potassium hydroxide (KOH 1M) as electrolyte solution [15]. Evidence of increased electric conductivity, facilitated EDL formation and negligible porous structure modification was found as consequence of Ni embedding. This results in the ability to synthesize carbon-based electrodes with tailored specific power and energy density by the accurate control of the amount of deposited Ni and C clusters. Embedded nickel has been also shown to promote the formation of ordered graphitic nanostructures in heated nanocomposites which critically increase the rate capability of the electrodes without reducing their volumetric energy density [15].

The embedding of nanoparticles in the carbon matrix via SCBD can be thus an effective method to significantly improve the ns-C electrochemical performances not only in terms of electrode conductivity but also electrolyte reversible absorption and pseudocapacitive behavior, opening the way for the synthesis of advanced capacitive materials with enhanced energy storage properties.

4 CONCLUSIONS

Supersonic cluster beam deposition (SCBD) is a high throughput technique for the integration of nanoparticles into almost any kind of substrate. The microfabrication of planar and flexible thin film supercapacitors by the SCBD method has been demonstrated. The synthesis of nanostructured porous carbon thin films via SCBD presents several advantages, such as the compatibility with temperature sensitive substrates and with standard planar microtechnology processes, that may be pivotal toward the development of miniaturized, planar and flexible supercapacitors. The relatively simple ns-C fabrication method and the high control over the deposited material properties (e.g. thickness, surface roughness , porosity and composition) obtained by the tuning of the deposition parameters empower the nanostructured carbon deposited by SCBD as an interesting material in electrochemical energy storage application especially where extremely thin films of material are requested or where fragile substrates (e.g. polymers) are needed.

REFERENCES

[1] Z.L. Wang, W. Wu. Angewandte Chemie 51, 11700–11721, 2012.
[2] M. Beidaghi, Y. Gogotsi. Energy Environ. Science, 7, 867-884, 2014

[3] J. Chmiola, C. Largeot, P. Taberna, P. Simon, Y. Gogotsi. Science 328, 480-483, 2010
[4] D. Pech, M. Brunet, H. Durou, P. Huang, V. Mochalin, Y. Gogotsi, P. Taberna, P. Simon. Nature Nanotechnology 5, 651–654, 2010.
[5] M.F. El-Kady, R. B. Kaner. Nature Communications 4, 1475, 2013.
[6] K. Wegner, P. Piseri, H.V. Tafreshi, P. Milani. Journal of Physics D: Applied Physics 39, R439-R459, 2006.
[7] K Wegner, S Vinati, P Piseri, A Antonini, A Zelioli, E Barborini, C Ducati, P Milani. Nanotechnology, 23, 185603, 2012
[8] G. Corbelli, C. Ghisleri, M. Marelli, P. Milani, L. Ravagnan. Advanced Materials 23, 4504–4508, 2011.
[9] G. Bongiorno, A. Podestà, L. Ravagnan, P. Piseri, P. Milani, C. Lenardi, S. Miglio, M. Bruzzi, C. Ducati. Journal of Materials Science: Materials in Electronics 17, 427-441, 2006.
[10] L.G. Bettini, G. Bardizza, A. Podestà, P. Milani, P. Piseri. Journal of Nanoparticle Research 15,1429-38, 2013.
[11] E. Barborini, P. Piseri P. Milani. Journal of Physics D: Applied Physics 32, L105-L109, 1999.
[12] P. Piseri, A. Podestà, E. Barborini, P. Milani. Review of Scientific Instruments 72, 2261-2267, 2001
[13] L.G. Bettini, M. Galluzzi, A. Podestà, P. Milani, P. Piseri. Carbon 59, 212-220, 2013.
[14] L.G. Bettini, P.Piseri, F. De Giorgio, C. Arbizzani, P. Milani, F. Soavi. Electrochimica Acta 2015 (accepted).
[15] L.G. Bettini, G. Divitini, C. Ducati, P. Milani, P. Piseri. Nanotechnology 25, 435401, 2014.