

## Electro-spun graphene-enriched carbon fibres with high nitrogen-contents for electrochemical water desalination



Yolanda Belaustegui<sup>a,1</sup>, Saioa Zorita<sup>a</sup>, Francisco Fernández-Carretero<sup>a</sup>, Alberto García-Luis<sup>a</sup>, Fabiola Pantò<sup>b</sup>, Sara Stelitano<sup>c</sup>, Patrizia Frontera<sup>d,e</sup>, Pierluigi Antonucci<sup>d,e</sup>, Saveria Santangelo<sup>d,\*,1</sup>

<sup>a</sup> Tecnalia Research & Innovation, Materials for Energy and Environment Area, E-48160 Derio, Bizkaia, Spain

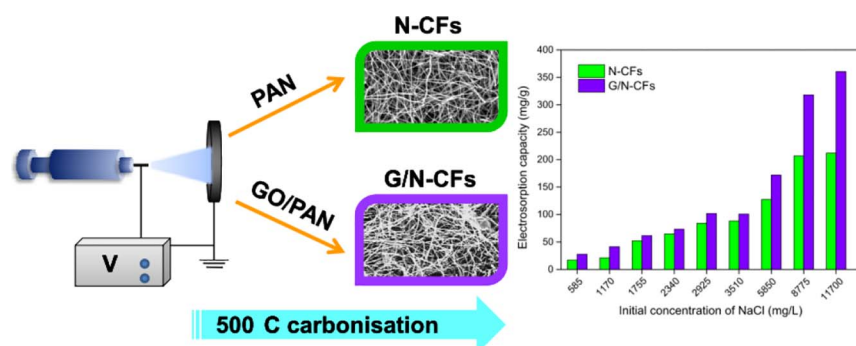
<sup>b</sup> Dipartimento di Ingegneria dell'Informazione, delle Infrastrutture e dell'Energia Sostenibile (DIIES), Università "Mediterranea", 89122 Reggio Calabria, Italy

<sup>c</sup> Dipartimento di Fisica (DF), Università della Calabria, 87036 Arcavacata di Rende, Italy

<sup>d</sup> Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università "Mediterranea", 89122 Reggio Calabria, Italy

<sup>e</sup> Consorzio Interuniversitario per la Scienza e la Tecnologia dei Materiali (INSTM), Firenze, Italy

### GRAPHICAL ABSTRACT



### ABSTRACT

Electro-spun carbon fibres doped with very high nitrogen concentrations (19–21 wt%) are obtained operating carbonisation at low temperature (500 °C). The as-synthesised fibres are evaluated as electrode materials for the electrochemical desalination of water. The effect of the enrichment of the nitrogen doped carbon fibres with thermally reduced graphene oxide is also investigated. The fibrous electrodes are able to remove amazing amounts of NaCl (17.0–27.6 mg/g) from a salty solution with an initial concentration of 585 mg/L. The nitrogen doping, which dramatically improves the wettability, plays a crucial role in determining the outstanding electro-sorption capacities of the fibres. It allows fully profiting of the more favourable pore size distribution in the graphene-enriched fibres, endowed with higher conductivity and capacitance, for the obtainment of unprecedented electro-sorption capacities via an extremely simple synthesis process, with no need of activation treatments.

\* Corresponding author.

E-mail address: [saveria.santangelo@unirc.it](mailto:saveria.santangelo@unirc.it) (S. Santangelo).

<sup>1</sup> Both authors contributed equally to this study.

## 1. Introduction

The ever-increasing demand of fresh water supply caused by increasing population and environmental contamination has encouraged the water desalination technologies worldwide to move forward in a cost-effective and energy-efficient direction [1]. The capacitive deionization (CDI) method, based on the formation of electrical double layers inside the pores of the electrode material [2,3], is one of the most attractive among them. CDI, also known as electro-sorptive desalination, is an environmentally friendly technology since no secondary contaminant is released during the process. CDI removes salts from water by using two oppositely charged carbon electrodes. On applying a voltage, the surface of the electrodes gets charged and an electrical double layer is formed between the electrode and the solution. These charged electrodes adsorb the counter ions present in the feed water on their pores and thereby, desalinate it. Once these pores are saturated with salt ions, the cell voltage is reduced, reversed or shorted to regenerate the electrodes and the previously stored ions are released into a waste water solution. The greatest advantage of CDI is its high theoretical energy efficiency for desalination [4]. For instance, the intrinsic energy required by CDI for brackish waters is  $\approx 0.1 \text{ kWh m}^{-3}$  [4], which is inferior to that of reverse osmosis ( $\approx 0.2 \text{ kWh m}^{-3}$ ), the most efficient technique presently available [1,4,5]. Another noteworthy advantage is its low equipment and operational costs because CDI is a low-pressure, non-membrane based desalination process that is controlled by a low applied voltage (0.8–1.2 V) and can be of great help in remote areas.

The CDI performance depends intimately on the physical and structural properties of the electrode materials. High specific surface area, high conductivity, and appropriate pore size distribution are basic electrode requirements [2,3]. In this scenery, carbon materials represent the ideal candidates as the CDI electrodes. Various nanocarbons, such as carbon nanotubes, carbon aerogel, mesoporous carbon, and activated carbon, have been successfully utilised to fabricate the electrodes in CDI cells [2,3,6].

Synthesising hybrid carbon nanostructures with tailored physical/chemical properties may represent the route to obtain engineered electrode materials with advanced electrochemical performances. A viable strategy contemplates the use of suitable additives. Thanks to its superior electronic conductivity and mechanical properties, graphene represents the ideal conductive additive for the fabrication of hybrid nanostructured electrodes [7]. Indeed, in spite of its worse performances, graphene oxide (GO) is routinely used in place of graphene [7,8] because of its better dispersibility in solvents, low-cost and large-scale production enabled by the chemical exfoliation method.

Several studies have demonstrated that doping carbon-based materials is a successful alternative strategy to tailor their physical/chemical properties [3,6,9–17]. It has been shown that the introduction of defects, heteroatoms and/or functional groups at the carbon surface can increase available active sites and enhance the reactivity and conductivity [12,14]. In particular, due to the presence of additional lone pairs of electrons, nitrogen atoms can provide carriers for the electronic conduction [6,9,18]. Actually, nitrogen-doped nanocarbons exhibit

improved electro-catalytic and electro-chemical properties [3,6,10–17]. Moreover, nitrogen doping has been recently shown to increase the wettability of the electrode materials by the electrolyte, resulting in the pseudocapacitive effect [3,6,16–18].

Specifically, in the field of CDI, from the porous electrode theory [2] it is well known that also intra-particle macro- and micro-pores of the electrode have influence over the effective concentration of the adsorbed salt. Electro-spinning (ES) is a very simple, scalable and inexpensive technique for the growth of one-dimensional nanostructures featured by hierarchical porosity (intertwined micro-, meso-, and macro-pores) [19–22]. Since the preparation of CDI electrode materials via ES occurs in two well distinct steps (namely, fibrous film deposition and thermal treatment of the as-spun film) there is the possibility of *continuously* depositing (over rotating drums) electro-spun fibres that will be thermally treated subsequently. This feature, together with its scalability, makes ES the most suitable technique for the large-scale production of CDI electrodes.

This contribution deals with synthesis, analysis and testing, as electrode materials in CDI cells, of electro-spun nitrogen-doped carbon fibres (N-CFs) and graphene-enriched nitrogen-doped carbon fibres (G/N-CFs), as obtained via thermal reduction of GO during the post-spinning fibre carbonisation step.

Nitrogen-doping of the electro-spun fibres can be very easily obtained by the use of a nitrogen-containing polymer, such as polyacrylonitrile,  $(\text{C}_3\text{H}_3\text{N})_n$ , featured by 26.4 wt% N-content, as a component of the spinnable solution. Previous studies have demonstrated that the nitrogen content of the heat-treated fibres decreases with increasing carbonisation temperature [22]. This is because, during the polymer carbonisation, cross-linking condensation reactions between two monomer units of the adjacent ladder polymeric molecular chains occur in the 300–500 °C temperature range, causing evolution of water vapour, whereas if the temperature further rises, also volatile nitrogen-containing by-products (such as hydrogen cyanide, HCN, and ammonia,  $\text{NH}_3$ ) are expelled from the fibres [23]. Therefore, in order to obtain fibres with high nitrogen-doping levels, in the present study, carbonisation temperature was set at 500 °C, the lowest value ever reported at the best of the authors' knowledge.

Dufficy et al. [15] have recently reported on the synthesis of composite anodes for lithium-ion battery consisting of carbon nanofibres containing thermally reduced graphene oxide. The fibres were prepared via ES followed by heat treatment at 650 °C, by dispersing in the spinnable solution different GO loads (1–20 wt%, relative to the polymer concentration), with 5 wt% GO load giving the best electrochemical performances. Based on these results, G/N-CFs were here prepared by the addition of 5 wt% GO to the spinnable solution. It has been proposed that removal of oxygen functional groups of GO occurs at temperatures as low as 200 °C, producing a defective  $\text{C } sp^2$  structure able to improve the electrical conductivity of the host amorphous matrix [15]. Thus, the incorporation of GO into the carbon fibres is expected to generate beneficial effects on their properties in spite of the low carbonisation temperature selected (500 °C). The performance of the produced materials was tested in the desalination of sodium chloride solutions by using CDI technology.

**Table 1**

Sample codes, composition of the spinnable solutions, results of the morphological analysis by SEM, and values of specific surface area (SSA), specific micro-pore volume (SMPV) and adsorption average pore size ( $d_p$ ). The fibre diameter range, as automatically calculated by the image analysis software, is reported;  $d_f$  stands for the value at which the diameter distribution is centred.

Sample code	Composition of the spinnable solution			SEM analysis results		SSA (m <sup>2</sup> /g)	SMPV (mm <sup>3</sup> /g)	$d_p$ (nm)
	PAN (wt%)	DMF (wt%)	GO (wt%)	$d$ range (nm)	$d_f$ (nm)			
N-CFs	6.50	93.50	0.00	135–1180	360	20.32	2.57	4.37
G/N-CFs	6.50	93.17	0.33	110–1070	340	16.76	1.29	4.62

Download English Version:

<https://daneshyari.com/en/article/7008090>

Download Persian Version:

<https://daneshyari.com/article/7008090>

[Daneshyari.com](https://daneshyari.com)