# Flexible Graphene-Enriched Fibrous Electrode Nanomaterials

*P. Frontera*[1], *F. Pantò*[1], *P.L. Antonucci*[1] *A. Malara*[2], *E. Fazio*[3], *F.Neri*[3], *S. Stelitano*[4],*and S. Santangelo*[1,*]

[1] Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università "Mediterranea", 89122 Reggio Calabria, Italy
[2] Dipartimento di Ingegneria dell'Informazione, delle Infrastrutture e dell'Energia Sostenibile (DIIES), Università "Mediterranea", 89122 Reggio Calabria, Italy
[3] Dipartimento di Fisica e di Scienze della Terra (DFST), Università di Messina, 98166 Messina, Italy
[4] Dipartimento di Fisica (DF), Università della Calabria, 87036 Arcavacata di Rende, Italy
*saveria.santangelo@unirc.it

Being endowed with extraordinary electrical and thermal conductivity, high surface area, good flexibility, superior chemical and thermal stability [1,2], graphene is often incorporated, as an additive, in composites containing all kinds of functional materials in order to improve their performances. As a matter of fact, the synthesis of new graphene-enriched (GE) nanomaterials for advanced applications is nowadays one of the areas of greatest interest for the Scientific Community. GE-nanomaterials are employed in a lot of different fields, including energy storage devices [3]. In this field, one of the most challenging tasks is the preparation of freestanding mats for the fabrication of flexible lithium ion batteries (F-LIBs).
Cobaltosic oxide ($Co_3O_4$) exhibits intriguing electronic, optical, electrochemical, and electrocatalytic properties. $Co_3O_4$-based composites have been considered as supercapacitors, heterogeneous catalysts, electrochemical sensors, and electrodes for F-LIBs [3,4].

This work deals with the preparation of freestanding mats of $Co_3O_4$-based GE-nanofibers (NFs) to be used as electrodes in F-LIBs. Synthesis is carried out by means of the electro-spinning (ES) that, thanks to its simplicity, cheapness, versatility and scalability, represents a very commercially-competitive technique for the growth of 1-dimensional materials [3,5,6].

Mats of $Co_3O_4$-based GE-NFs were prepared by using *N*,*N*-dimethylformamide (DMF) as solvent, polyacrylonitrile (PAN, $(C_3H_3N)_n$) as polymer and graphene oxide (GO) as carbonaceous additive. Cobalt acetate (CA, $CH_3COO)_2Co\cdot 4H_2O$) or cobalt nitrate (CN, $Co(NO_3)_2$) was used as a cobalt oxide precursor, and its influence on the morphology of the spun material was investigated. The spinnable solution was prepared by dissolving PAN (6.5 wt%) in DMF, adding the cobalt precursor (CA or CN, 2.5 wt%), and stirring until a clear solution was obtained. Finally, 1 wt% GO was incorporated into the mixture and stirred. A 20 ml syringe, equipped with a 40 mm long 0.8 mm gauge stainless steel needle, was used. Solution feeding-rate, applied potential and distance between the tip of the syringe needle and the grounded aluminum collector were 1.41 ml/h, 15 kV and 15 cm, respectively. ES was carried out at 20±1°C (relative humidity: 40%).

CN gave rise to fluffy deposits, while the use of CA allowed for the formation of films. As-spun films were calcined in air for 6 h at different temperature (225 and 300°C) to obtain the oxide from the precursor, and then annealed in inert environment (helium) at 600°C for 2 h to carbonize the polymer [6].
Figure 1 shows the main results of Raman and x-ray photoelectron spectroscopy (XPS) analyses. The $Co_3O_4$ crystalline phase of the oxide forms at any calcination temperature ($T_C$). Degradation of PAN-component of the NFs at higher $T_C$ causes the relative weight of the cobaltosic oxide to increase from ~25wt% to ~70wt% and the C$sp^2$ Raman signal to weaken.
Figure 2 shows the most representative results of scanning electron spectroscopy/energy-dispersive x-ray spectroscopy (SEM/EDX). Thermal treatments do not alter the fibrous structure of the as-spun mats. Nonetheless, at higher $T_C$ (Figs. 2a–2b) the average diameter of

the fibers (420–300 nm) depends on their composition and shrinks in the presence of $Co_3O_4$ and GO. Instead, by calcining at 225°C (Figs. 2c–2e) the average fiber diameter (420 nm) does not vary with the fiber composition. The elemental dispersion, as detected by EDX, is generally homogeneous (Fig. 2f).

Summarizing, flexible freestanding mats of $Co_3O_4$-based GE-NFs mats (inset of Fig. 2e) are obtained by the use of CA as precursor and 6 h calcination in air at 225°C followed by 2 h annealing in He at 600°C. They will be tested as anodes materials for F-LIBs.

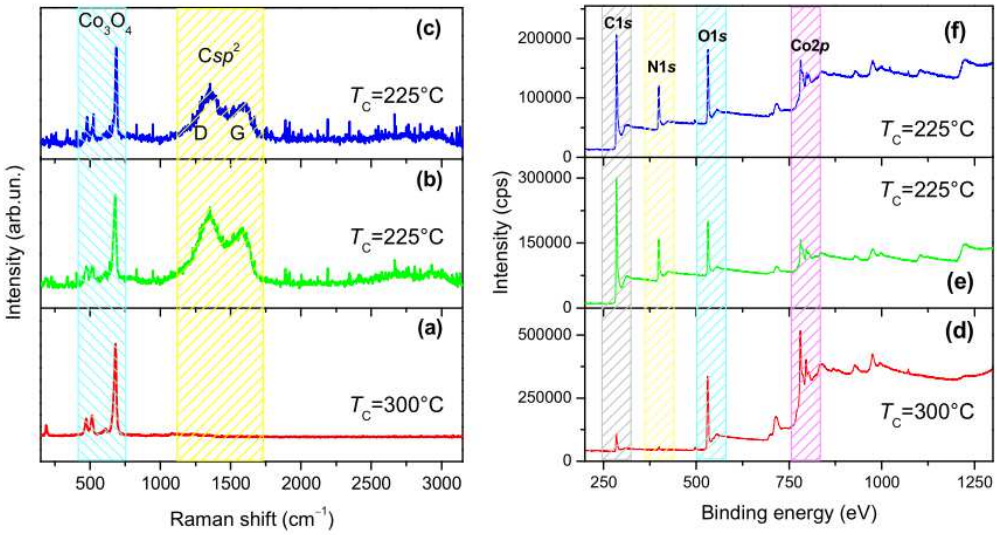


Figure 1: (a–c) Raman and (d–f) XPS spectra of $Co_3O_4$-based NFs (a,b,d,e) and $Co_3O_4$-based GE-NFs (c,f) obtained for $T_C$=300°C (a,d) and $T_C$=225°C (b,c,e,f).

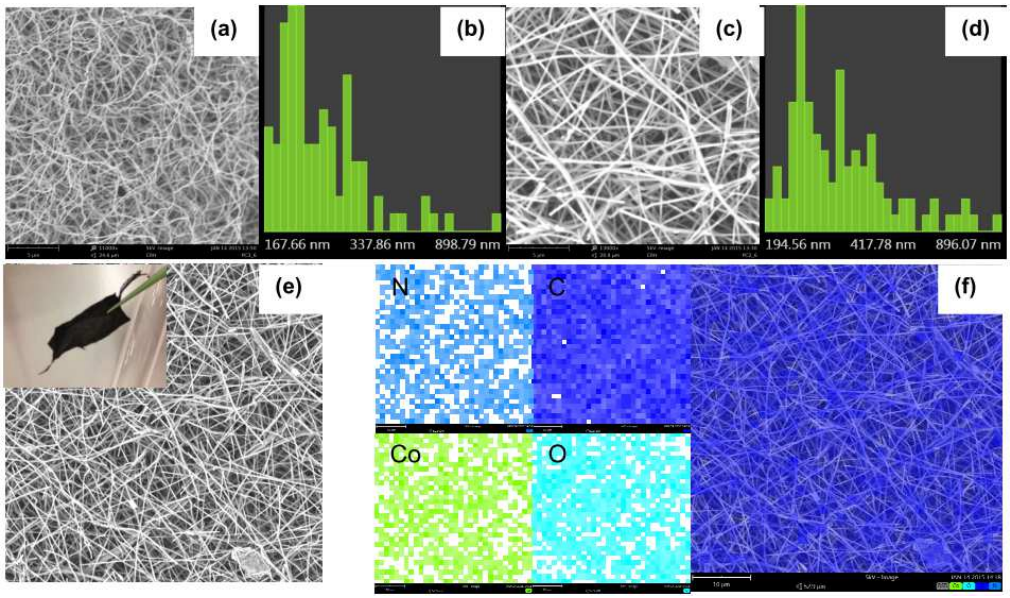


Figure 2: (a,c,e) SEM images of $Co_3O_4$-based NFs (a,c) and $Co_3O_4$-based GE-NFs (e) obtained for $T_C$=300°C (a) and $T_C$=225°C (c,e). The NF diameter distributions (b,d) for cases (a) and (b), as well as the elemental dispersion resulting from EDX in case (e) are also shown.

## References


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