Supplementary materials

Effect of germanium incorporation on the electrochemical performance of electrospun Fe_2O_3 nanofibers-based anodes in sodium-ion batteries

Beatrix Petrovičovà[1], Chiara Ferrara[2,3,*], Gabriele Brugnetti[2], Clemens Ritter[4], Martina Fracchia[5], Paolo Ghigna[5], Simone Pollastri[6], Claudia Triolo[1,3], Lorenzo Spadaro[7], Riccardo Ruffo[2,3], Saveria Santangelo[1,3,*]

[1] Dipartimento di Ingegneria Civile, dell'Energia, dell'Ambiente e dei Materiali (DICEAM), Università Mediterranea di Reggio Calabria, 89122 Reggio Calabria, Italy; beatrix.petrovicova@unirc.it (B.P.); claudia.triolo@unirc.it (C.T.)
[2] Dipartimento di Scienza dei Materiali, Università di Milano Bicocca, 20125 Milano, Italy; g.brugnetti@campus.unimib.it (G.B.); riccardo.ruffo@unimib.it (R.R.)
[3] National Reference Center for Electrochemical Energy Storage (GISEL) - Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali (INSTM), 50121 Firenze, Italy
[4] Institut Laue-Langevin - 71 avenue des Martyrs CS 20156, 38042 Grenoble, Cedex 9, France; ritter@ill.fr (C.R.)
[5] Dipartimento di Chimica, Università degli studi di Pavia, 27100, Pavia, Italy; martina.fracchia02@universitadipavia.it (M.F.); paolo.ghigna@unipv.it (P.G.)
[6] Elettra-Sincrotrone Trieste, 34149, Basovizza, Trieste, Italy; simone.pollastri@elettra.eu (S.P.)
[7]Istituto di Tecnologie Avanzate per l'Energia (ITAE) del Consiglio Nazionale delle Ricerche (CNR), 98126 Messina, Italy; lorenzo.spadaro@itae.cnr.it (L.S.)

* Correspondence: chiara.ferrara@unimib.it (C.F.); saveria.santangelo@unirc.it (S.S.)

Preparation of the Electrospun NFs

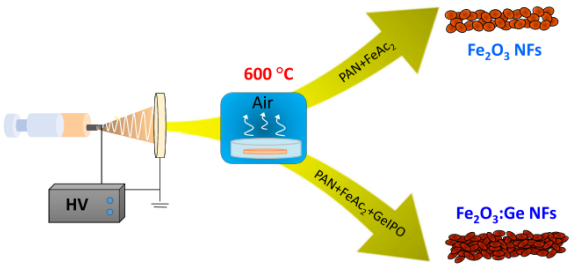

Figure S1. Sketch of the synthesis route followed to produce the electrospun iron oxide NFs.

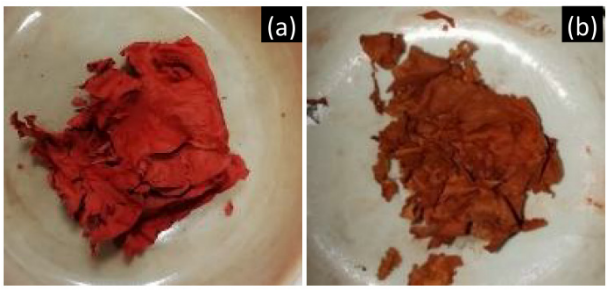

Figure S2. Photo of the as-calcined (a) Fe_2O_3 and (b) Fe_2O_3:Ge NFs. The different colour hints at the formation of a different crystalline phase when germanium is incorporated.

Physicochemical Properties of the NFs

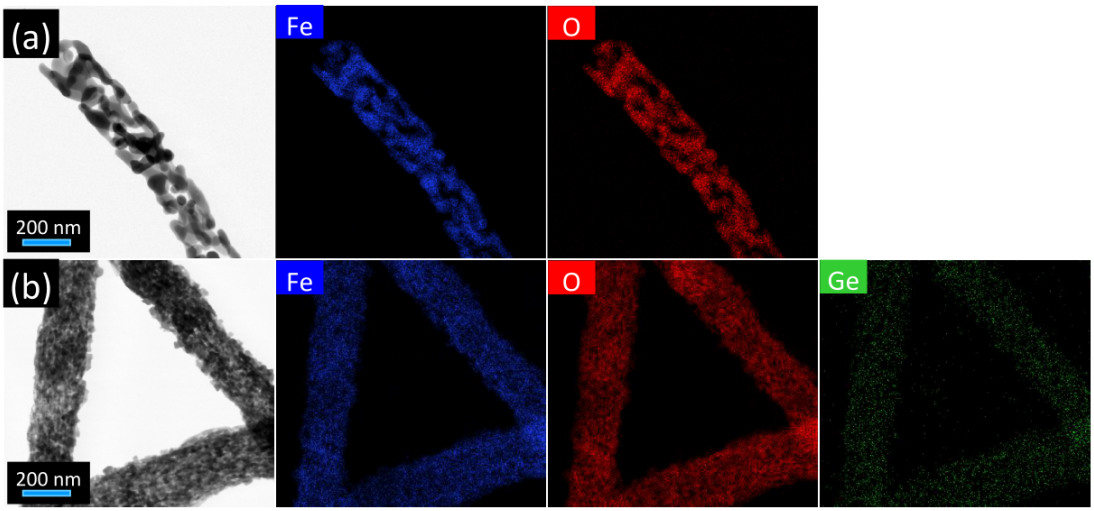

Figure S3. Elemental composition of the NFs (from HRTEM/EDX analysis). (a) Fe_2O_3 NFs and (b) Fe_2O_3:Ge NFs.

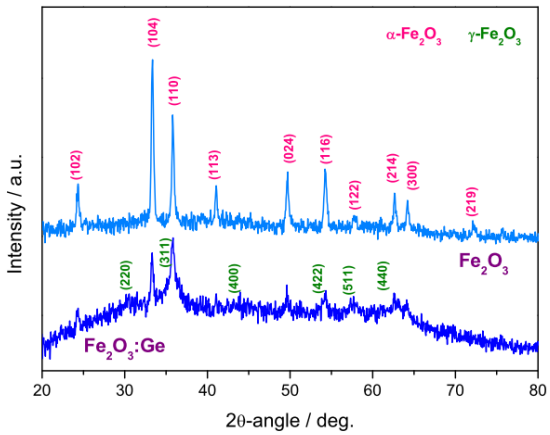

Figure S4. XRD patterns of the investigated NFs.

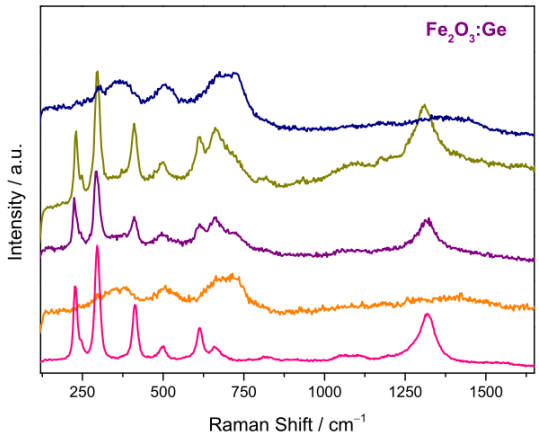

Figure S5. Micro-Raman spectra, as measured at different random locations in the sample. The incorporation of germanium reflected into a spatial inhomogeneity of the NFs, owing to the co-existence of α- and γ-polymorphs of the oxide.

Table S1. Surface composition of the NFs.

Sample	Fe / at%	O / at%	Ge / at%
Fe_2O_3 NFs	30.4	69.6	0.0
Fe_2O_3:Ge NFs	20.2	68.8	11.0

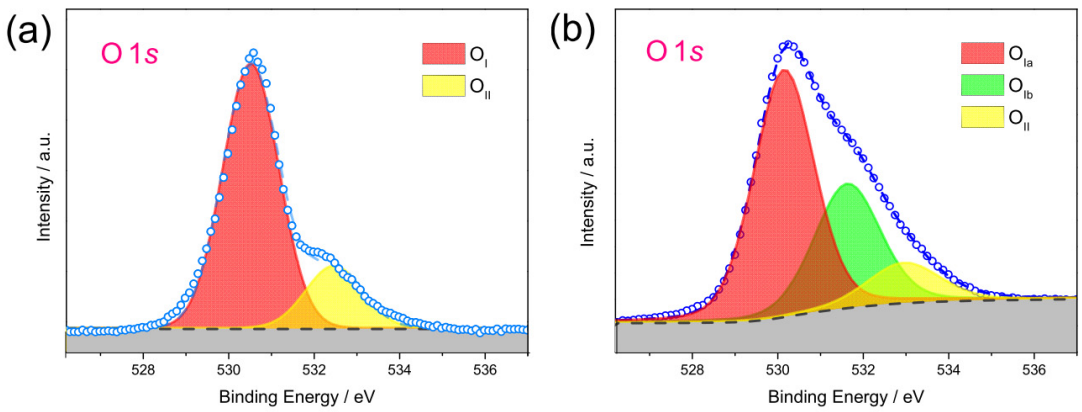

Figure S6. Deconvolution of the O 1*s* core level profiles of (a) Fe_2O_3 NFs and (b) Fe_2O_3:Ge NFs.

Table S2. Binding energies (in eV) and fractional area of the components of O 1*s* core level in the NFs.

Sample	O 1s					
	O_{Ia}		O_{Ib}		O_{II}	
	BE / eV	Area / %	BE / eV	Area / %	BE / eV	Area / %
Fe_2O_3 NFs	530.54	83.2			532.41	16.8
Fe_2O_3:Ge NFs	530.15	57.6	531.64	31.4	532.66	11.1

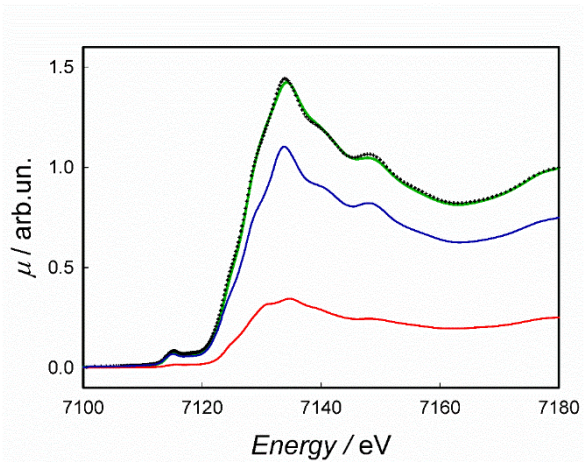

Figure S7. Linear combination fit of the spectrum of Fe_2O_3:Ge NFs acquired at the Fe K-edge. The green line represents the experimental signal, while the black dots represent the fit obtained with 77% of maghemite and

23% of hematite. The spectra of maghemite and hematite, weighed for 0.77 and 0.23, respectively, are shown as a blue and red line.

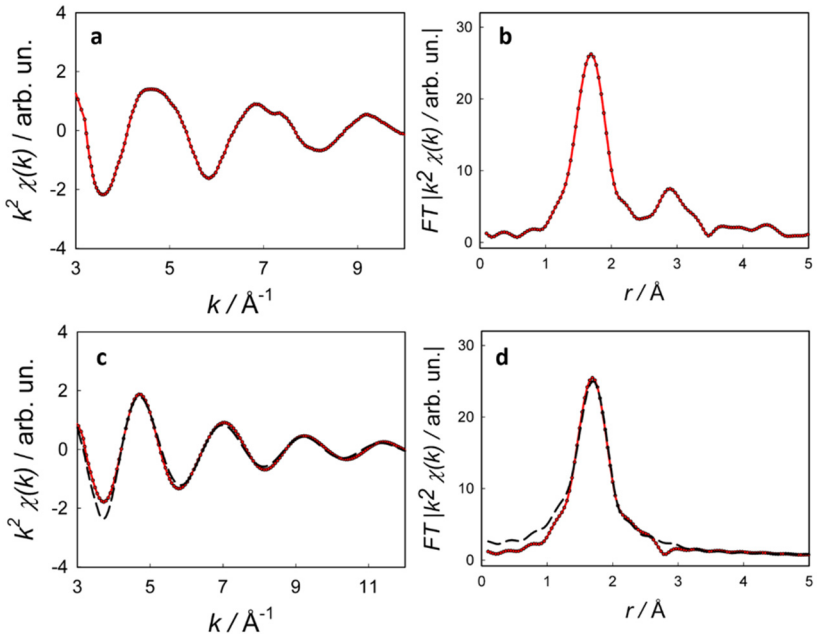

Figure S8. (**a**) EXAFS signal and (**b**) Fourier transform for the spectrum of Fe_2O_3:Ge NFs at the Ge K-edge. The EXAFS and the Fourier transform after the Fourier filtering are shown in panel (**c**) and (**d**), respectively. The red line represents the experimental signal, while the black dotted line is the theoretical fit obtained starting from the GeO_4 structural model.

Table S3. Refined parameters obtained after the refinement of the Fourier-filtered signal. The goodness of fit (GOF), valuated through the F factor ($F = 100 \sum_i^N \frac{[\chi_{i,exp} - \chi_{i,calc}]^2}{\sigma_i}$) , is 5.2%.

Shell	N	Atom	R(Å)	σ^2 (Å^2)
1	4	O	1.771(6)	0.0051(6)

Electrochemical Properties of the NFs

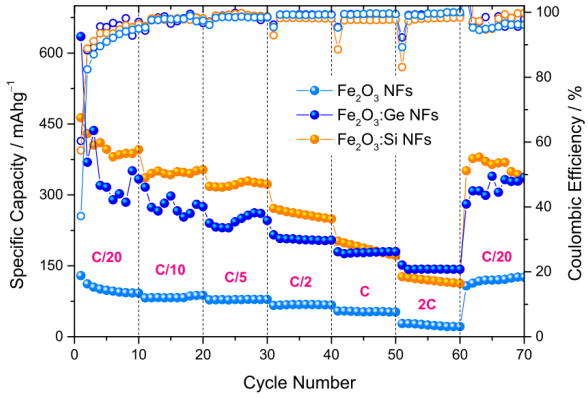

Figure S9. Results of the rate capability test on Fe_2O_3:Ge NFs, compared with previously investigated Fe_2O_3 and Fe_2O_3:Si NFs [S1].

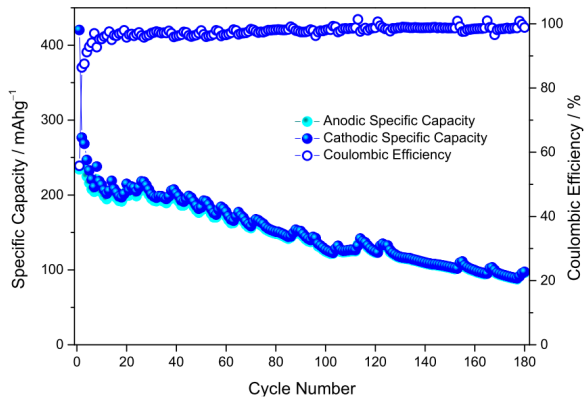

Figure S10. Results of the cyclability test on Fe_2O_3:Ge NFs.

S1. Fiore, M.; Longoni, G.; Santangelo, S.; Pantò, F.; Stelitano, S.; Frontera, P.; Antonucci, P.L.; Ruffo, R. Electrochemical characterization of highly abundant, low cost iron(III) oxide as anode material for sodium-ion rechargeable batteries. *Electrochim. Acta* **2018**, *269*, 367–377.