Experimental report

14/07/2021

Proposal: **EASY-641** **Council:** 4/2020

Title: Fe oxides as negative electrodes for rechargeable batteries: long vs short range structure

Research area: Materials

This proposal is a new proposal

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Experimental team:

Local contacts: Clemens RITTER

Samples: doped Fe2O3

Instrument	Requested days	Allocated days	From	To
D20	6	6	23/08/2020	24/08/2020

Abstract:

Fe2O3 is evaluated as conversion anode material for Na ion batteries but presents some drawbacks: poor electronic transport properties and large volume changes during charge/discharge processes. The strategy adopted here is the production of Fe2O3 nanofibers doped with Mg, Mg/Ti, Ge. The modification of the morphology can improve the cyclability; the doping with aliovalent cations can modify the crystal and electronic structure. Our preliminary electrochemical tests are promising for the Ge composition; XAS data have already been acquired on the Fe-,Ti-, and Ge- edge and evidence significant differences in the samples’ structure. At the same time, the long-range order on these materials is unclear as the investigation and resolution of different Fe-O polymorphs with the use of XRD techniques is hardly feasible. The collected XRD patterns shows significant differences but they are compatible with different structural models. For this reason, we apply for the EASY Access program to collect room temperature data of the three samples (0.5g each) on the D20 beamline ensuring suitable condition to investigate the crystal structure, substitution, occupancies of these oxides.

Proposal – EASY 641 - Fe oxides as negative electrodes for rechargeable batteries: long vs short range structure

The aim of this experiment was the investigation of doped Fe_2O_3, considered as possible anode material for sodium-ion batteries [1,2]. Fe_2O_3 is a conversion type material, presenting high theoretical capacity but suffering of some serious drawback such as the poor electronic transport properties and large volume variation and cracking during charge/discharge cycles. The strategy adopted by our group to mitigate these hurdles is the production of Fe_2O_3 in form of nanofibers considering aliovalent doping; the most successful doping in term of improvement of the electrochemical performances has been obtained with the use of Ge in Ge:Fe mass ratio of 1:9 (corresponding to 0.085 Ge:Fe molar ratio). The nanofibers have been successfully obtained through the use of electrospinning preparation (see Figure 1). Indeed, the control of the morphology can improve the cyclability of the material and the doping with aliovalent cations can modify the crystal and electronic structure, facilitating the transport properties. This material has been tested as anode for sodium ion batteries and it shows good specific capacity (320 mAh g^{-1} at 50 mA g^{-1}) with good rate capability (140 mAh g^{-1} at 2 A g^{-1}).

With the aim to investigate the structure of this system and account for the doping effect of the structure (e.g. doping site, structural distortion and/or phase transition induced by substitutions) X-ray absorption (XAS) measurements (Figure 2) and neutron diffraction data have been collected. The use of neutron scattering technique is necessary as the Fe-O systems are known for the polymorphism (hematite, magnetite, maghemite). Nevertheless, these structures differ for the occupancy of different sites and vacancies ordering thus the solely use of X-ray diffraction (XRD) is not sufficient for the careful evaluation of such structural aspects as the analysis of such data are compatible with different structural models.

Neutron powder diffraction data have been collected on the D20 beamline at room temperature using vanadium sample holder with 1.54 Å wavelength in the 0-150° angular range using high resolution option; data were analyzed using the FullProf Suite to perform LeBail fitting and traditional Rietveld refinements.

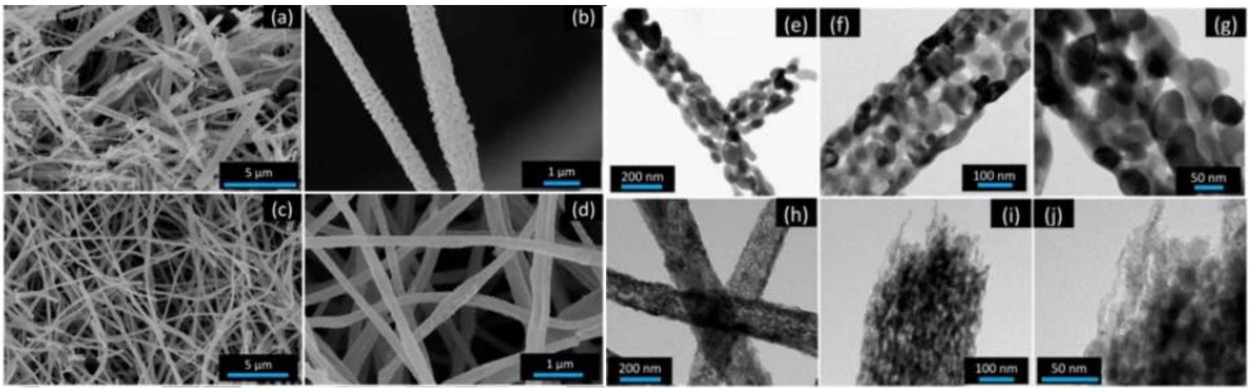

Figure 1 SEM images (a-d) and TEM images (e-g); SEM images (a,b) of the Fe_2O_3 reference compound and (c,d) for the Ge:Fe_2O_3 system; TEM images (e-g) of the Fe_2O_3 reference compound and (h-j) for the Ge:Fe_2O_3 system.

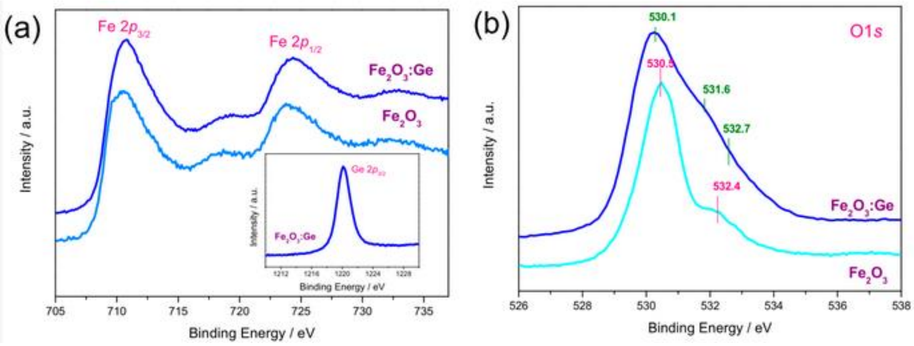

Figure 2 – X-ray absorption spectra of the Fe 2p (a) and O 1s (b) core levels for both Fe_2O_3 and Ge:Fe_2O_3 compositions; in the insert the Ge 2p core level for the doped system.

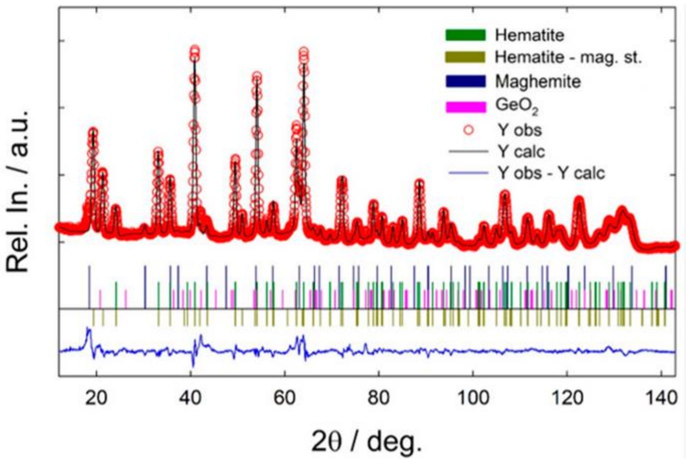

Figure 3 – Rietveld refinement of the powder diffraction pattern of Ge:Fe_2O_3 system (Chi2 = 22.0, R_p, 1.97, R_{wp} = 2.39); phase composition has been identified: hematite 91.1%, maghemite 8.6 %, GeO2 0.3%

The neutron pattern has been fitted considering the presence of hematite and maghemite; the observed strong extra reflections (17-27° angular range, 51°) are associated with the magnetic structure of hematite [3]. This magnetic structure was considered in the refinement as an independent phase [4], see Figure 3.

Combining the information from XAS analysis and from neutron refinements, the phase composition of the systems was determined. The α-Fe_2O_3 and γ-Fe_2O_3 have been identified as the dominant phases, the presence of an amorphous component must be inferred. The Ge is accommodated in the tetrahedral sites of the maghemite structure; the hematite phase could also accept Ge dopant, probably on the defective surface sites as no GeO_6 species (that should be associated to the bulk α-Fe_2O_3) have been detected. The observed improved electrochemical performances of the Ge:Fe_2O_3 with respect to the Fe_2O_3 (both in form of nanofibers) have been associated to the synergistic effect between nanostructured morphology and electronic transport properties of the doped composition.

The analysis of the EASY experiment, together with the other data, have been reported in following scientific publication:

B. Petrovicova, C. Ferrara, G. Brugnetti, C. Ritter, M. Fracchia, P. Ghigna, S. Pollastri, C. Triolo, L. Spadaro, R. Ruffo, S. Santangelo, *Effect of Germanium Incorporation on the Electrochemical Performances of Electrospun Fe_2O_3 Nanofibers-Based Anodes in Sodium-Ion Batteries*, App. Sci, 2021 11(4) 1483

Bibliography

[1] Qi, S.; Xu, B.; Tiong, V.T.; Hu, J.; Ma, J. Progress on iron oxides and chalcogenides as anodes for sodium-ion batteries. Chem. Eng. J. 2020, 379, 122261.

[2] 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.

[3] Hill, A.H.; Jiao, F.; Bruce, P.G.; Harrison, A.; Kockelmann, W.; Ritter, C. Neutron diffraction study of mesoporous and bulk hematite, α-Fe2O3. Chem. Mater. 2008, 20, 4891–4899.

[4] Ritter, C. Neutrons not entitled to retire at the age of 60: More than ever needed to reveal magnetic structures. Solid State Phenom. 2011, 170, 263–269.