Highly Stable Fe$_3$O$_4$/C Composite: A Candidate Material for All Solid-State Lithium-Ion Batteries

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Highly Stable Fe₃O₄/C Composite: A Candidate Material for All Solid-State Lithium-Ion Batteries

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Fe₃O₄ nanoparticles synthesized by a base catalyzed method are tested in an All-Solid-State (ASLB) battery using a sulfide electrolyte. The pristine nanoparticles were morphologically characterized showing an average size of 12 nm. The evaluation of the electrochemical properties shows high specific capacity values of 506 mAhg⁻¹ after 350 cycles at a specific current of 250 mAg⁻¹, with very high stability and coulombic efficiency.

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The large development of Li-ion technology allows for a massive spreading of portable electronics, as well as for a progressive diffusion of electric vehicles (EV). However, the increasing demand for battery systems with higher energy density requests a breakthrough in finding new materials. In the last decade, the industry standard has been represented by insertion materials for both anode and cathode, while recently alloy-forming materials with Li, Z (Z = Si, Sn, Sb, Bi) formula have emerged as viable, alternative anodes. In addition, recently a new chemistry has surfaced, allowing to store more Li⁺ by the so-called conversion mechanism. In this process the active material is reversibly reduced into metallic nanoclusters embedded in a Li₂O matrix, following the general Eq. 1:

$$M_nO_y + 2ye^- + 2yLi^+ \leftrightarrow xM^0 + yLi_2O$$  [1]

Among the others, several transition metal oxides, sulfides, nitrides, phosphides and fluorides have been explored and tested as conversion anodes. Considering 3d-transition metal oxides, iron oxides α-Fe₂O₃ and Fe₃O₄ have received great attention.

Fe₃O₄, also known as magnetite, is a low cost, environmentally benign metal oxide that can undertake a reversible conversion reaction with Li⁺ ions, according to Eq. 2 which results in a theoretical capacity of 924 mAhg⁻¹, almost 3 times higher than the commercially available graphite anode:

$$Fe_3O_4 + 8e^- + 8Li^+ \leftrightarrow 3Fe^0 + 4Li_2O$$  [2]

Despite these premises, transition metal oxides associated with the conversion mechanism usually suffer from a series of issues intimately connected with the conversion reaction itself. In fact, remarkable structural changes and volume expansion are associated with this mechanism, eventually leading to pulverization and loss of contact between active material particles and the current collector, which result in poor electron and ion transport limiting the overall cycle-life.

In order to improve the electrochemical performance, different approaches have been proposed: firstly, the use of composite nanoarchitectures with optimized morphologies, such as nanorods, hollow or nano-spheres, and carbon coating strategies; lastly, the use of graphene to form composites showed remarkable improvements in terms of cycle-life.

Here, we report the synthesis, characterization and evaluation of the electrochemical properties of pristine Fe₃O₄ nanoparticles synthesized from a base catalyzed method mechanically mixed with electrosyn polymer Polyacrylonitrile (PAN) derived carbon fibers as simple composite material. The Fe₃O₄/C electrodes are characterized by galvanostatic cycling experiments using currents as high as 2000 mA g⁻¹, revealing high capacity values and capacity retention, together with a very good capacity recovery during the rate capability experiment.

Experimental

Fe₃O₄ nanoparticle synthesis and characterization.—Fe₃O₄ nanoparticles were synthesized using a previously reported method: 1.0 g of FeCl₂·4H₂O and 2.7 g of FeCl₃·6H₂O were dissolved in 20 ml of distilled H₂O each, in two separate containers. The solutions were then mixed, and 100 ml of a 1.5 M solution of NH₄OH were added at room temperature. Finally, 30 ml of a 25% w/w solution of NH₄OH were added to the reaction mixture. The resulting dispersion was kept under reflux for 18 h and cooled down to room temperature. The resulting nanoparticles were recovered, rinsed three times with distilled H₂O and ethanol, and finally dried under vacuum at 50 °C.

The micro-nanofibers carbon mats were prepared through an electrosprinning process. The polymer blend was prepared dissolving Polyacrylonitrile (Mw = 150000, Aldrich) in N,N-dimethylformamide (DMF, Aldrich). The solution was stirred for 20 h at 60 °C on a heating plate. The solution was electrosprun at constant flow rate of 0.60 ml h⁻¹ and with a DC voltage of 15–18 kV. Relative humidity and environmental temperature were 20% and 30 °C, respectively. The needle was placed at 15 cm distance from the plate collector (covered with an aluminum foil), at 10° of inclination angle. Electrospun mats were thermally treated, under air flow, with a heating rate of 5 °C min⁻¹, at 250 °C for 1 h. Thermal reduction was performed at 700 °C under Ar:H₂ flow (95:5, 200 ml min⁻¹) at a
heating rate of 10 °C min⁻¹ to 400 °C and then 5 °C min⁻¹ to 700 °C with a final plateau of 3 h. The Fe₂O₃/C composite was then prepared by directly ball-milling iron oxide particles and the PAN derived carbon nanofibers at 250 rpm for 1 h, using ZrO₂ spheres and a Retsch PM100 instrument. The Fe₂O₃/C ratio was 80:20.

The Fe₂O₃/C powder was characterized by means of X-ray diffraction (XRD) using a Rigaku Ultima diffractometer (Cu Kα = 1.540 Å). X-ray photoelectron spectroscopy (XPS) data were acquired using a PHI 5800, Physical Electronics instrument, under Ar atmosphere, using Al Kα radiation (200 W, 13 kV), at a pressure of 10⁻⁹ Torr. The diameter of the analyzed surface was 800 μm. The spectra were calibrated by the binding energy of the C 1s peak (BE = 284.5 eV). All spectra were fitted by the deconvolution software Casa XPS (Casa Software). Gaussian-Lorentzian (30% Gaussian) functions and a Shirley-type background were employed in all fitting spectra. SEM micrographs were recorded on a ZEISS LEO 1550 instrument, equipped with a X-MAXN EDX detector by Oxford Instruments. Transmission electron microscopy experiments have been carried out using a FEI Tecnai 200 kV cryo-TEM instrument. TEM pictures have been analyzed using the ImageJ software.25 In particular simulated electron diffraction patterns have been reconstructed by performing a Fast-Fourier Transform (FFT) analysis of selected areas of the micrographs using the routines embedded in the ImageJ code. TEM samples have been prepared by suspending the powders in acetone by sonication: the suspension has been dropped on holey carbon grids and directly transferred into the microscope. Thermogravimetric analysis (TGA) has been performed with a Mettler-Toledo TGA/SDTA 851 instrument, in air atmosphere, in a temperature range of 25 °C–900 °C with a heating ramp of 10 °C min⁻¹.

**Cell assembly and electrochemical tests.**—The electrode powder was prepared by ball milling the active material, the solid-state electrolyte and carbon nanofibers (CNF) as conductive additive, in the 35 (Nanocomposite): 60 (Solid Electrolyte): 5 (CNF) proportion, respectively, at 250 rpm for 10 min. Solid state torque cells were assembled in Ar-filled glovebox (MBraun): 200 mg of a Ar-filled glovebox (MBraun): 200 mg of a 35 (Nanocomposite): 60 (Solid Electrolyte): 5 (CNF) proportion, respectively, at 250 rpm for 10 min. Solid state torque cells were assembled in Ar-filled glovebox (MBraun): 200 mg of a Ar-filled glovebox (MBraun): 200 mg of a

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**Results and Discussion**

**Structural and morphological characterization.**—The Fe₂O₃/C composite was characterized using different techniques. Figure 1 reports the thermogravimetric analysis (TGA) and the X-ray Diffraction (XRD) spectra. Thermogravimetric analysis, Fig. 1a, shows a small weight loss, around 5%, up to 100 °C, due to volatile species and moisture residues in the sample. The progressive weight decrease, leading to a sharp loss at 400 °C, due to the conversion of carbon materials to CO₂, accounts for a total of 25% weight loss, which excludes moisture at the beginning, is in line with the Fe₂O₃/C proportions of the prepared composite. It is worth noting that the composite powders were always dried at 120 °C for 12 h under vacuum before moving them into the glovebox to assemble the torque cells.

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**Figure 1.** (a) Thermogravimetric analysis of the Fe₂O₃/C composite material (b) X-ray diffraction pattern of Fe₂O₃ nanoparticles, reference main peaks are indexed according to the Crystallography Open Database (COD) database.

The XRD pattern of the pristine magnetite powder, Fig. 1b, shows a series of peaks related to Fe₂O₃ diffraction (Crystallography Open Database (COD), card no. 00-152-8612). The small size of each crystallite is estimated as ~12.60 nm using Rietveld refinement (Maud software suite).26 Rietveld data is shown in Table S1.

Figures 2a–2d reports the SEM images of pristine powder. The morphology of Fe₂O₃ is characterized by spherical shaped nanosized crystallites, aggregated in bigger secondary particles, without any peculiar feature. The electrospun polyanionitrolite (PAN) derived carbon nanofibers are shorter than usual, due to the mechanical milling step during the preparation of the composite material. Fe₂O₃ nanoparticles result to be in close contact with the electrospun carbon fibers, thus the overall electronic conductivity is expected to be improved. Additional micrographs of the PAN-derived carbon nanofibers are reported in Fig. S1 (available online at stacks.iop.org/JES/167/070556/mmedia), detailing the difference in the pristine state, and after the ball milling.

The nanomorphology of the composite material has been investigated by TEM (see Figs. S2–S3) and conforms the observation by SEM. Despite the formation of aggregates, probably due to magnetic stirring during the synthetic procedure, the nanoparticles have a spherical shape with the boundaries of each single crystallite still visible, as can be seen in Fig. S1, reporting the HR-TEM micrographs. The large carbon matrixes are surrounded and decorated by dark nanoparticles, partially agglomerated. The FFT analysis of a selected area shown in the Fig. S3c is presented in the Fig. S3d. The simulated electron diffraction image confirms the identification of randomly oriented nanocrystals of magnetite Fe₂O₃, with e565 structure.27,28 The crystallite size is evaluated in the range of 6 nm–13 nm (Fig. 1b), consistent with the value calculated by applying the Scherrer’s equation.

X-ray photoelectron spectroscopy (XPS) analysis is performed to better understand the composition of the iron-based composite. The survey spectrum reported in Fig. 3a reveals the presence of Fe, O and C. The Fe 2p core level, Fig. 3b, shows different peaks which can be fitted with two spin–orbit doublets and a shakeup satellite. The doublets are related to the presence of Fe³⁺ and Fe²⁺. The results are consistent with the reported values for Fe₃O₄.26,27 The O 1s spectrum, Fig. 3c, is deconvoluted into two peaks, the main one at 530 eV is due to the presence of Fe₂O₃ species and can be attributed to Fe₂O₃ while the other peak at 531.1 eV is attributed to the presence of residual oxygen-containing groups in the sample.

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(e.g. O–H etc...) which, in turn, could induce a small shift in the Fe$^{2+}$ and Fe$^{3+}$ related doublets. The C1s core level, Fig. 3d, shows three peaks at 284.7, 286.2 and 289 eV related to C–C and C–O species as residual products from the synthesis of the electrode powder.

**Electrochemical characterization.**—Electrochemical characterization using solid state electrolyte is performed by means of several techniques to have a wider picture on the cycling behavior and electrochemical performance. Cyclic voltammetry, Fig. 4, in the potential range 0.100 V–3.000 V at 0.050 mVs$^{-1}$ scan rate, evidences several electrochemical signals: during the first cathodic sweep, three peaks, at 1.66 V, 1.10 V and 0.70 V respectively, are visible. The peak at 1.66 V (indicated as * in Fig. 4) has been observed also by other authors: it describes a still not completely clear irreversible process only occurring during first discharge. The peak at 1.10 V is consistent with the pre-lithiation of the iron oxide phase, in which Li$^{+}$ ions are inserted into the spinel crystalline structure of Fe$^{3}$O$_{4}$ according to the reaction:

$$\text{Fe}_3\text{O}_4 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{Fe}_3\text{O}_4$$  \[3\]

The peak at 1.10 V (A) is consistent with the pre-lithiation of the iron oxide phase, in which Li$^{+}$ ions are inserted into the spinel crystalline structure of Fe$^{3}$O$_{4}$, according to the reaction:

Then, the sharp peak at 0.70 V (B), describes the first-cycle reduction of the oxide nanoparticles to Fe metal by the conversion reaction, leading to the formation of an amorphous composite of Fe$^{3}$ dispersed in a Li$_2$O matrix.

In the first anodic sweep a shoulder labeled as (C) is visible at E = 1.15 V, was assigned to Li$^{+}$ deinsertion from the PAN-derived carbon nanofibers, then a couple of broad and partially overlapped peaks are visible at 1.58 V and 1.82 V (D), which are attributed to the oxidation of the Fe$^{0}$ nanoparticles to Fe$^{2+}$ and Fe$^{3+}$, respectively. These results are consistent with literature data reported for liquid systems. In the following cathodic sweep a pronounced hysteresis appears, following a well-known electrochemical behavior typical for conversion anode materials, and the peak (B) shifts to 0.8 V, now labeled as peak (D). On the other hand, the anodic oxidation process, peak (D), remains substantially unchanged. From Cycle#2, another electrochemical process is activated at E = 2.45 V and was labeled as (E). It is of interest to investigate the presence of an additional reversible redox couple related to peak (E), visible in the successive voltammetry cycles, and labeled as peaks F and G, respectively, see Fig. S2. Galvanostatic cycling were performed using a current of 250 mA g$^{-1}$ (current density 0.32 mA cm$^{-2}$) in the voltage range between 0.100 V < E < 3.000 V, the same used for the cyclic voltammetry experiment, to ensure both reproducibility and to limit Li$^{+}$ insertion into the PAN-derived carbon fibers at very low potentials.

The obtained results are reported in Fig. 5. The panel (a) reports the prolonged cycling performance of the Fe$^{3}$O$_{4}$ nanoparticles highlighting a first discharge capacity of 1049 mAhg$^{-1}$ and a subsequent charge at 643 mAhg$^{-1}$, with coulombic efficiency around 61%. The first-cycle irreversible capacity is attributed to irreversible processes which could be associated to the formation of a passivation layer on the active material particles, as already evidenced by the CV experiment of Fig. 4. During the following 15 cycles, the capacity is stabilized at around 506 mAhg$^{-1}$ for the remaining 335 cycles, with coulombic efficiency steadily exceeding 99.5%.

The galvanostatic E vs Q profiles of the first discharge step, Fig. 5b, reveal two short sloping plateaus at 1.93 V and 1.65 V, a short sloping plateau at 1.02 V, and a larger one at 0.76 V. The profile associated with the subsequent charge step presents a sloping plateau which extends from 1.5 V to 1.90 V. The profiles are almost consistent with the cycling voltammetry experiment. From the second charge/discharge cycle, any sign of definite plateaus disappears in favor of a more sloped line around 1.0 V during the discharge steps, and from...
1.6 V to 1.75 V during the charge steps. Additionally, with increasing cycle number a reversible short sloping plateau is visible at 2.45 V, which is assigned to a broad potential interval in which can be present both the Li₂S and the Li₃PS₄ electrochemical reactions. Furthermore, the presence of a Li₂S related peak, could be associated with some amorphous unreacted Li₂S, left over during the electrolyte ball-milling preparation step and introduced into the electrode composite formulation mixture. This behavior has not been fully understood yet. The data showed in Fig. 5b, is even clearer in the differential plots shown in Fig. 5c, in which all the signals present in the cyclic voltammetry are present, showing a highly stable and reversible behavior up to cycle 300.

![Figure 3. X-Ray Photoelectron Spectroscopy characterization of Fe₃O₄ composite material: (a) Survey spectrum (b) Experimental and fitted plot of the Fe2p core level. (c) Experimental and fitted plot of the O1s and (d) C1s core levels.](image)

![Figure 4. Cyclic Voltammetry of Fe₃O₄. Scan rate: 0.050 mVs⁻¹. Working potential range: 0.001 V < E < 3.000 V.](image)

![Figure 5. Cycling behavior of Fe₃O₄/PAN cell at 250 mAg⁻¹ specific current. 0.100 V < E < 3.000 V. (a) Charge/discharge capacity; (b) E vs Q profiles of selected cycles; (c) calculated dQdE differential plots.](image)
The large voltage hysteresis after the first discharge and visible changes in the shape of voltage profiles, are typical features of conversion materials. This has been reported by several authors, associating parallel-occurring processes, such as: (I) the increase in surface area in Fe3O4 nanoparticles-based electrodes during the first discharge, with the pristine oxide to the Li2O/M composite formation40; (II) possible different reaction pathways during the conversion reaction.41,42

Rate capability tests for the Fe3O4/C composite using different current rate, ranging from 100 mA g\(^{-1}\) to 2000 mA g\(^{-1}\) are reported in Fig. 6 and detailed in Table I. The delivered capacity ranges from 984 mAh g\(^{-1}\) at 100 mA g\(^{-1}\) to 236 mAh g\(^{-1}\) at 2000 mA g\(^{-1}\), while, the ability to recover the original specific capacity is evaluated after 150 cycles at 250 mA g\(^{-1}\). Average reversible capacity values of 660 mAh g\(^{-1}\) were obtained, with a coulombic efficiency constantly exceeding 99.8%, see Table I. Specific capacity profiles of the rate capability test are shown in Fig. S4. At higher currents, the profiles become almost featureless, and this polarization effect could hint at a slower kinetic response of the conversion mechanism for stronger polarizations.

The good performance at high current rate and the outstanding electrochemical stability in the following 150 cycles at lower current rate, in which most of the original specific capacity is recovered, is due to different factors. First, the very small size of active material particles and the fibrous nature of the carbon material create a high conducting network favoring electronic transport. Secondly, the preparation procedure through ball milling of both the composite material and the electrode powder mix ensures a very close contact among the composite nanoparticles, the solid-state electrolyte and the conductive additive which benefit to the Li\(^+\) diffusion and charge transfer kinetics.

Further extended galvanostatic cycling experiments were conducted using two high current-rate of at 500 mA g\(^{-1}\) (current density 0.65 mA cm\(^{-2}\)) and 1000 mA g\(^{-1}\) (current density 1.31 mA cm\(^{-2}\)) for over 1000 cycles, with the aim to check the prolonged stability of the solid-state cell, which are depicted in Fig. 7. In both experiments, the system shows an impressive cycling stability by reaching 1000 cycles mark without any failure. Considering the current rate of 500 mA g\(^{-1}\), marked as (a) in the graph, the electrode highlights a capacity retention of 39.10% at the last cycle and an average capacity value of 240 mAh g\(^{-1}\), while for the experiment at 1000 mA g\(^{-1}\), marked as (b), the electrode has a capacity retention of 51.46% during the last cycle and an average capacity value of 193 mAh g\(^{-1}\).

![Figure 6](image6.png)

**Figure 6.** Rate capability experiment of Fe3O4/C electrodes in solid state configuration cell. Current rate from 100 to 2000 mA g\(^{-1}\) and voltage range 0.100 V < E < 3.000 V.

![Figure 7](image7.png)

**Figure 7.** Extended galvanostatic performance of Fe3O4/C cells comparison; 0.100 V < E < 3.000 V (a) \(I_{\text{spec}} = 500\) mA g\(^{-1}\); (b) \(I_{\text{spec}} = 1000\) mA g\(^{-1}\).

![Figure 8](image8.png)

**Figure 8.** Nyquist plots of Fe3O4/C all-solid-state cell. Bias potential of 3.000 V, frequency range of 100 KHz < f < 100 mHz; Oscillation Amplitude \(\Delta E = \pm 5\) mV.

| Specific Current/mA g\(^{-1}\) | Current Density/ma cm\(^{-2}\) | Capacity/mAh g\(^{-1}\) |
|-----------------------------|-----------------------------|-------------------------|
| 100                         | 0.13                        | 984                     |
| 200                         | 0.26                        | 777                     |
| 500                         | 0.65                        | 606                     |
| 1000                        | 1.31                        | 396                     |
| 2000                        | 2.62                        | 236                     |
| 250                         | 0.32                        | 662 (avg.)              |

**Table 1.** Rate capability experiment specific capacity values at the different specific currents.
consistent electrochemical features with the rest of the electrochemical characterization.

Nyquist plots, in Fig. 8, have been acquired after full charge (3,000 V) by EIS measurements at selected cycle numbers (1, 5, 10, 50, 100, 200). All the EIS spectra are characterized by very large depressed semicircles in the medium frequency range, related to charge transfer processes (see in inset of Fig. 8), and a sloping line at low frequency related to diffusion processes. As a general trend, the overall impedance of the electrodes tends to a slight increase upon cycling. At the same time, an increase of impedance values upon cycling, mostly during the initial cycles, is a signal of a worsening of cycling. LiBs with improved cycle-life and safety.

Conclusions

Fe3O4 nanoparticles have been synthesized by a simple base-promoted method, and mechanically mixed with PAN derived electrospun carbon nanofibers. The characterization was performed using different techniques while the electrode powders have been prepared by ball milling of the composite material with Li2PS4-Li sulfide solid-state electrolyte and conductive carbon additive. Their electrochemical characterization revealed a very stable cycling performance. Nyquist plots, in Fig. 8, have been acquired after full charge (3,000 V) by EIS measurements at selected cycle numbers (1, 5, 10, 50, 100, 200). All the EIS spectra are characterized by very large depressed semicircles in the medium frequency range, related to charge transfer processes (see in inset of Fig. 8), and a sloping line at low frequency related to diffusion processes. As a general trend, the overall impedance of the electrodes tends to a slight increase upon cycling. At the same time, an increase of impedance values upon cycling, mostly during the initial cycles, is a signal of a worsening of cycling. LiBs with improved cycle-life and safety.

Acknowledgments

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