



Short communication

Electrochemical characteristics of iron oxide nanowires during lithium-promoted conversion reaction



Inchul Hong^a, Marco Angelucci^b, Roberta Verrelli^a, Maria Grazia Betti^c, Stefania Panero^a, Fausto Croce^d, Carlo Mariani^c, Bruno Scrosati^e, Jusef Hassoun^{a,*}

^a Dipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 2, I-00185 Roma, Italy

^b Dipartimento di Fisica, Sapienza Università di Roma, P.le A. Moro 2, I-00185 Roma, Italy

^c Dipartimento di Fisica, CNISM, CNIS, Sapienza Università di Roma, P.le A. Moro 5, I-00185 Roma, Italy

^d Dip. Farmacia, Università "G.D'Annunzio", Via dei Vestini 31, 66100 Chieti, Italy

^e Elettrochimica ed Energia, Via di Priscilla 22, I-00199 Roma, Italy

HIGHLIGHTS

- Iron oxide nanowires are characterized as anode material for lithium-ion battery.
- The anode has specific capacity of 800 mAh g⁻¹ evolving at 0.9 V vs. Li.
- Morphological and structural variation during lithium-conversion process is studied.
- The material has low cost and environment compatibility.

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ABSTRACT

Iron oxide nanowires are synthesized and characterized as negative electrode for lithium ion battery. The lithium-conversion reaction of the material is studied by electrochemical techniques as well as by XRD and SEM. Lithium cells based on the electrode material evidence a reversible capacity of about 800 mAh g⁻¹ and a multiple-step electrochemical process leading to the formation of amorphous compound. Furthermore, SEM analysis of the compound formed by direct lithium atoms deposition on the iron oxide nanowires clearly evidences the change of the electrode morphology upon formation of a lithiated phase. We believe that the data here reported may shed light on the properties of the iron oxide nanowires as high capacity anode for lithium ion battery.

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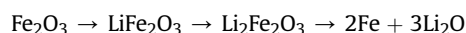
1. Introduction

Recently, the development of alternative anode materials of enhanced capacity and safety level assumed key role in the development of high performance lithium ion batteries. Transition metal oxides, based on the conversion reaction with lithium, are among the most promising alternatives to the graphite conventionally used as anode in commercial lithium ion battery [1] that is nowadays considered the best candidate to fulfill the strict requirements of emerging applications such as hybrid and electric cars and energy plants [2].

The conversion mechanism involves the exchange of more than one electron for redox center, thus allowing a higher

specific capacity and energy density in comparison with the conventional electrodes based on lithium ions intercalation/de-intercalation. Among the various transition metal oxides, Iron (III) oxide Fe₂O₃ has attracted great interest in this field of research not only due to its good electrochemical properties (i.e. theoretical specific capacity of 1007 mAh g⁻¹) but also due to its very low cost and eco-sustainability [3]. In lithium cell, Fe₂O₃ electrode reacts through a complex mechanism consisting in the progressive intercalation of lithium ions in the three-dimensional electrode structure and, subsequently, in the conversion of Fe₂O₃ to metal Fe and Li₂O.

Considering the cell discharge process, the Fe₂O₃ electrochemical reaction can be described, according to literature papers [4], by the following steps:



* Corresponding author.

E-mail address: jusef.hassoun@uniroma1.it (J. Hassoun).

The overall electrochemical process implies the exchange of 6 electrons for redox center and, therefore, a value of specific capacity much higher than the one shown by conventional anodes (i.e. 1007 mAh g⁻¹ for Fe₂O₃ and 370 mAh g⁻¹ for graphite).

However, Fe₂O₃ and other conversion electrodes are still far from being implemented as anodes in lithium ion batteries due to several problems limiting their performances in practical cells [5]. Structural re-organization experienced by the electrode during conversion reaction leads to de-cohesion and segregation of the Fe and Li₂O phases and, in the worst cases, to the pulverization of the electrode. This issue implies unsatisfactory charge–discharge efficiency of the cell and low capacity retention over cycling. In order to overcome these limits and make the transition metal oxide a viable electrode for lithium ion battery application many efforts have been recently made, mainly within the material engineering research field. A promising solution to reduce the volume changes of the electrodes during the electrochemical process consisted is the addition of a buffer matrix to the active material. It has also been demonstrated that the oxide particle size and morphology strongly influence the electrode behavior in practical cells [6] and, therefore, many attempts have been addressed to the synthesis of size controlled transition metal oxide particles of different shapes [7,8]. Here we report the electrochemical study of a Fe₂O₃ – nanowires electrode with the aim of testing its applicability in lithium ion batteries and of shedding light on its reaction mechanism by using both electrochemical techniques, such as galvanostatic cycling, potentiodynamic cycling and voltammetry, and chemical–physical techniques such as XRD and SEM.

2. Experimental

Hard template, mesoporous silica (SBA-15) was synthesized by the sol–gel method using a nonionic surfactant (EO₂₀PO₇₀EO₂₀). SBA-15 was synthesized by the sol–gel method using a nonionic surfactant, EO₂₀PO₇₀EO₂₀ (EO and PO denote the ethyleneoxide and propyleneoxide unit, average Mw = 5800, Aldrich). Tetraethyl orthosilicate was added to the surfactant aqueous solution in which the pH was adjusted to 1.0 using 36% HCl. The mixture was then stirred at 35 °C for 24 h, and kept in a convection oven at 80 °C for 24 h. The reactant was filtrated, and the precipitate was annealed at 600 °C in a muffle. For embedding Fe₂O₃ in mesoporous silica, Fe(NO₃)₃·9H₂O 0.01 M was dissolved in 50 ml of ethanol and added to 1 g of SBA-15. The slurry was stirred at room temperature and then dried at 40 °C for 1 week. The so obtained brown colored powder was sintered at 550 °C for promoting NO_x decomposition and dehydration. The powder was following etched by 2 M NaOH solution for 6 h, washed and filtered several times. Finally, pure nanowires-agglomeration of Fe₂O₃ (following called with the acronym NWF) was obtained after drying at 60 °C.

The NWF anodes were prepared as thin films by casting on copper support a slurry composed by the active material (80% wt), PVdF 6020 Solvay binder (10% wt) and MMM Belgium Super-P carbon electronic conducting additive (10% wt).

XRD measurements were performed using a Rigaku D-max X-ray diffractometer equipped with a Cu-K α radiation source. The Rietveld refinement of the XRD electrochemical data was performed by using the data analysis program MAUD. The fitting of the experimental pattern has been performed by considering the hematite (JCPDS # 86-2368) and maghemite (JCPDS # 24-0081) Fe₂O₃ phases. The fitting procedure was characterized by an acceptable RW agreement factor (<20%). The phase ratio has been determined as a result of this Rietveld analysis.

Swagelok t-type lithium half cells were assembled using a lithium metal foil counter electrode and a Whatman™ separator

soaked with 1 M LiPF₆ Ethylene Carbonate–Dimethyl Carbonate (EC:DMC = 1:1 Merk Battery Grade) electrolyte solution.

The galvanostatic cycling tests were performed in the voltage range 0.3 V–3 V vs Li⁺/Li using a Maccor 4000 series Battery Test System.

Cyclic Voltammetry (CV) tests were performed using lithium half cells with a lithium metal reference electrode at a scan rate of 0.1 mV s⁻¹ within the 0.3–3 V vs. Li⁺/Li potential range using a Bistat Biologic-Science Instruments potentiostat–galvanostat. All

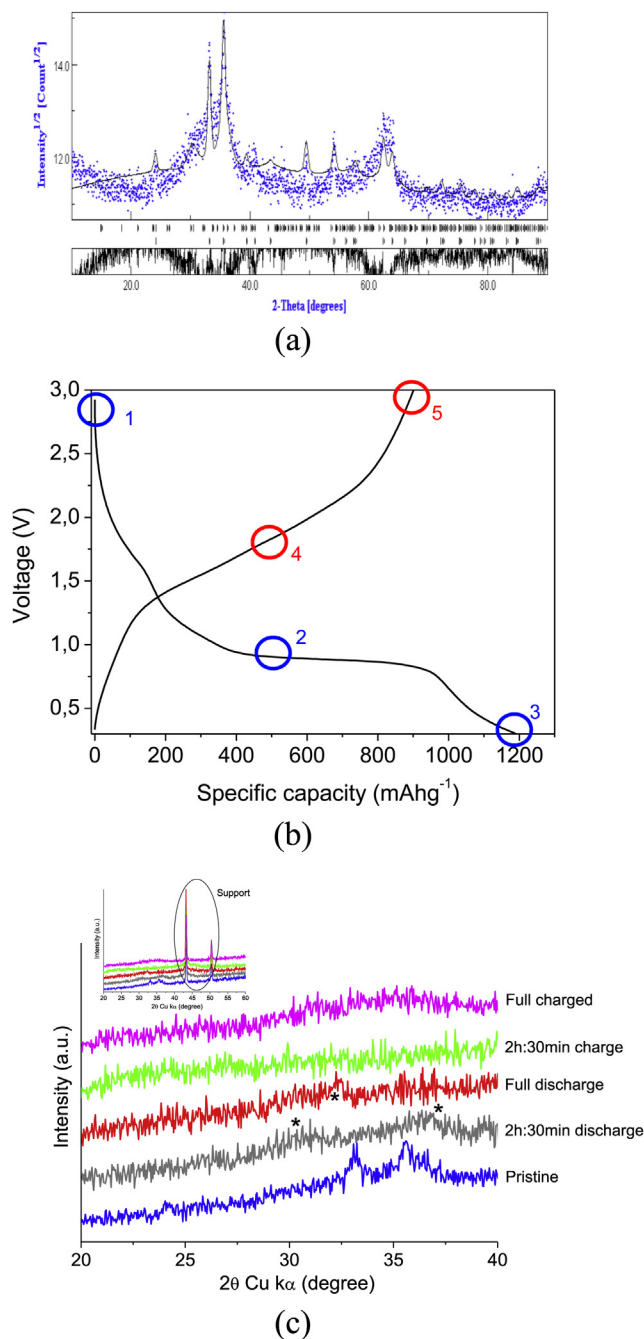


Fig. 1. (a) NWF powder experimental XRD pattern (blue) and computed spectra (black) obtained by the Rietveld refinement of diffraction data. (b) Voltage vs. specific capacity profile of the Li/EC:DMC, LiPF₆ 1M/NWF cell and (c) ex-situ XRD patterns of the corresponding NWF electrode upon cycling, within inset the signals of the electrode current collector. Voltage range 0.3–3 V, C/5 rate ($C_{\text{theoretical}} = 1007 \text{ mAh g}^{-1}$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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