



Ionic liquid assisted solid-state synthesis of lithium iron oxide nanoparticles for rechargeable lithium ion batteries



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ABSTRACT

The solid-state reaction of iron oxide, lithium carbonate and the ionic liquid 1-Ethyl-3-methylimidazolium acetate leads to the formation of lithium iron oxide (LFO). This synthesis is a simple way to realize particles in a range of 200 nm to 10 μm. Varying the temperature of the solid-state reaction is possible to control the surface and morphology of the LFO particles. The material can be processed in water for the realization of composite anodes suitable for use in lithium ion batteries. The LFO-based anodes, which feature the typical behavior of conversion electrodes, might display high specific capacity and decent cycling stability.

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1. Introduction

Lithium-ion batteries (LIBs) are presently seen as one of the most important electrochemical storage devices [1,2]. In the last years tremendous efforts have been made to increase the performance as well as the safety of LIBs leading to the consideration of a large variety of active materials. Among the materials investigated so far, metal oxides (M_xO_y , $M = Cu, Fe, Co, Ni, \text{etc.}$) are considered as one of the most interesting for the realization of advanced anodes [3–5]. M_xO_y belong to the so-called conversion materials. During electrochemical cycling the reduction of M_xO_y to metal (M) and lithium oxide (Li_2O) takes place, followed by the more or less reversible oxidation of M to M_xO_y , or a slightly different oxide. Typically, M_xO_y -based anodes display a specific capacity significantly higher than those of the state-of-the-art anode material graphite [3,6]. However, their stability over cycling is lower than that of graphite [6,7].

Among the M_xO_y investigated in the past years, $\alpha\text{-Fe}_2\text{O}_3$ can be considered one of the most attractive [5]. As a matter of fact $\alpha\text{-Fe}_2\text{O}_3$ displays a high theoretical capacity (1007 mAh g^{-1} [6]), is abundant, environmentally friendly, safe and inexpensive [5,6]. Because of these appealing features, large research efforts have been dedicated to the synthesis and use of this metal oxide in LIBs [6,8–11]. Although important achievements have been obtained along the years, still many efforts

seem to be necessary for the introduction of this material in commercial devices. Particularly, the poor energy efficiency and poor reversibility of the charge–discharge process appear important aspects, which should be addressed. The initial poor efficiency of this material, but more in general of all metal oxides, is typically attributed to the formation of the Solid Electrolyte Interphase (SEI) generated by the electrolyte decomposition [5,12]. In a recent publication, however, we showed that also the formation of cubic $\alpha\text{-LiFeO}_2$ (LFO) during the first lithiation–delithiation process of carbon coated $\alpha\text{-Fe}_2\text{O}_3$ might reduce the initial efficiency of this metal oxide. Since the formation of LFO reduces the amount of lithium available for the following charge–discharge process, the presence of LFO reduces also the capacity that can be delivered by the electrodes [10]. Nevertheless, it is interesting to notice that once the LFO is formed, the reversibility of the lithiation–delithiation process might increase and the electrodes can deliver a stable capacity [10].

To the best of our knowledge, in the past the research in LFO was mainly focused in the use of this material as a cathode [13–17] and only a publication considered LFO-based anodes for LIB [18]. Considering the abovementioned finding, however, an investigation about the behavior of LFO-based anode appears justified. As a matter of fact, if this type of anodes would show good cycling stability, their use could be of interest.

In this manuscript we report about the synthesis of carbon coated LFO nanoparticles and their use as anode in LIBs. Initially, a novel ionic liquid assisted synthesis for carbon coated LFO nanoparticles is described. Afterwards, the morphological and structural characterization of these nanoparticles is investigated. Finally, the electrochemical performance of LFO-based anodes is considered.

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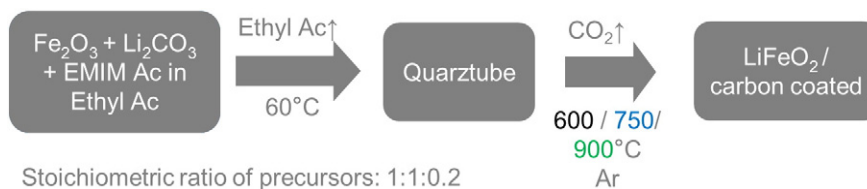


Fig. 1. Reaction scheme.

The aim of this work is to characterize the influence of the solid state synthesis temperature on the morphology, carbon coating and resulting electrochemical behavior, to identify the optimal α -LiFeO₂ for use as an anode material in lithium ion batteries.

2. Experimental

2.1. Synthesis of lithium iron oxide

A solid state reaction was used to synthesize LiFeO₂ (LFO). Fe₂O₃ and Li₂CO₃ with the molar ratio 1:1 were ground. 0.2 M of the ionic liquid 1-Ethyl-3-methylimidazolium acetate (EMIM Ac) was solved in ethyl acetate and added to the mixture of Fe₂O₃ and Li₂CO₃. To reach a uniform ionic liquid wetting of the precursors, the mixture was stirred for one hour at 5000 rpm (Dremel 4000, Dremel, Austria). Afterwards the mixture was heated for 12 h at 60 °C to remove the ethyl acetate. The precursors were inserted in a quartz tube reactor inside a horizontal furnace (Type: P330, Nabertherm, Germany) and heated up to 600 °C, 750 °C and 900 °C (heating rate: 4.9 °C min⁻¹) in constant flow of pure argon for 24/48 h. Fig. 1 gives an overview of the synthesis process. All synthesized LFO were characterized “as synthesized”. The samples synthesized at 750 °C and 900 °C were also ball milled with a planetary ball mill (speed of the main disk: 343 rpm, speed of the planets: 85.75 rpm for 4 h) prior to characterization.

2.2. Morphological, structural and electrochemical characterization

High resolution scanning electron microscopy (HRSEM) and powder X-ray diffraction (XRD) were used to identify the morphology and crystal structure of the materials. The HRSEM measurements were performed using a ZEISS Auriga® microscope, the XRD measurements

were carried out using a Bruker D8 Advance diffractometer (Cu-K α -radiation, $\lambda = 0.154$ nm). The specific BET surface area of the material was determined with the ASAP 2020 equipment from Micromeritics Instrument Corporation (USA). To get information about the carbon content a CHN (carbon, nitrogen, hydrogen) quantitative elemental analysis was performed.

The synthesized LFO nanoparticles were used for the realization of composite electrodes as described in ref [6]: 85 wt.% active material LFO, 10 wt.% conductive additive (Carbon black Super C65) and 5 wt.% of binder (Na-CMC, Walocel CRT 2000 PPA 12 from Dow Wolff Cellulosics). The mass loading of the electrode active material ranged between 1 and 2 mg cm⁻². The macroscopic electrode area was 1.13 cm². The theoretical capacity (848 mAh g⁻¹) utilized for the definition of 1C was calculated assuming a full delithiation of the α -LiFeO₂.

The electrochemical performance of the composite electrode was tested using a 3-electrode cell configuration. In these tests, lithium iron phosphate (LFP, Süd-Chemie) or metallic lithium foils (Rockwood Lithium) were used as counter electrodes; lithium foil was also used as a reference electrode. The electrolyte of choice was of 1 M LiPF₆ (SigmaAldrich) in propylene carbonate (PC, UBE, Japan). 120 μ l of electrolyte were drenched in the separator Whatman GF/D glass microfiber filter (thickness: 675 μ m, diameter of 13 mm).

The galvanostatic cycling (GC) were carried out using a Maccor series 4300 battery tester (Maccor, Inc., USA). The cyclic voltammeteries (CV) were performed on a VMP multichannel potentiostatic-galvanostatic system (Biologic Science Instrument, France). All potentials shown in this work refer to the Li/Li⁺ couple.

3. Results and Discussion

3.1. Characterization of carbon-coated lithium iron oxide

The solid-state reaction of iron oxide, lithium carbonate and EMIM Ac leads to the formation of lithium iron oxide. The LiFeO₂ synthesis route shows very high yield (>98%), leading to a porous black powder. The different reaction temperatures led to, mainly, α -LiFeO₂. The XRD diffraction patterns of the prepared materials are in a good agreement with the literature data of cubic α -LiFeO₂ (Space group 225, Fm-3 m) [19] with cell parameters of $a = 0.416$, $b = 0.416$, $c = 0.416$ nm. The reflections at 37.4°, 43.5°, 63.2°, 75.8° and 79.8°, respectively, match to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) planes of the rock salt structure of cubic α -LiFeO₂, thus confirming that the synthesis of this compound was successful. As visible in Fig. 2, the LFO synthesized at 600 °C for 24 h have broader and less intense diffractions, due to their lower crystallinity, compared to the other materials. However, reflections of unreacted precursors Li₂CO₃ and Fe₂O₃ can be identified in its diffraction pattern. Increasing the reaction time to 48 h, while keeping

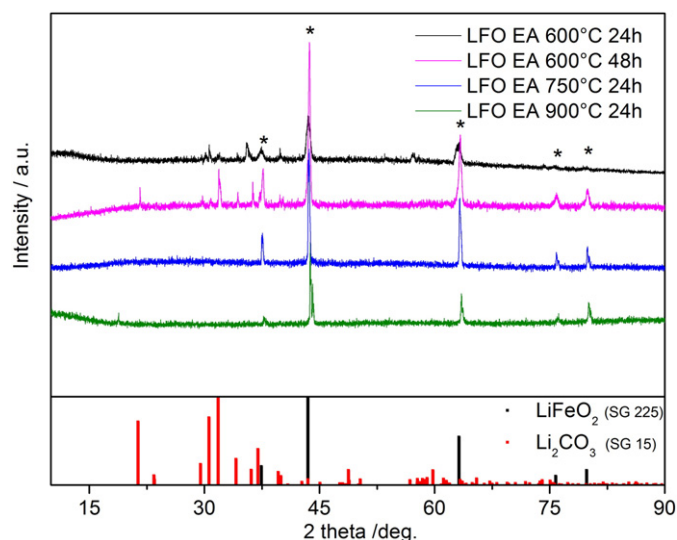


Fig. 2. XRD pattern of LFO materials synthesized at different temperatures; the symbol (*) is indexing the main reflections of LFO. At the bottom of the figure the index LiFeO₂ and Li₂CO₃ are reported. (ICSD-PDF No of the literature: LiFeO₂ (01-070-2711 17-938); Li₂CO₃ (01-087-0728 22-1141).

Table 1
Crystal size along different crystallographic directions for α -LiFeO₂ according to Scherrer's equation [21,22].

	600 °C 24 h	600 °C 48 h	750 °C 24 h	900 °C 24 h
$D_{(1\ 1\ 1)}/\text{nm}$	14.81	35.08	29.08	35.39
$D_{(2\ 0\ 0)}/\text{nm}$	13.94	32.22	38.46	34.11
$D_{(2\ 2\ 0)}/\text{nm}$	11.85	27.11	31.21	31.85

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