

A composite electrode based on sub-micrometric iron metal and lithium fluoride



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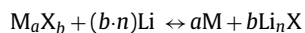
ABSTRACT

In this paper a general method to obtain a mixture of a transition metal embedded in a matrix of lithium fluoride is proposed. The method consists in the reduction of the oxide of the transition metal with lithium hydride to form the correspondent transition metal and lithium oxide. This latter is then converted into lithium fluoride by solid state reaction with ammonium fluoride. In this work the proposed method was applied to iron(III) oxide to obtain a mixture of iron metal and lithium fluoride. The crystal structure and phase purity of the intermediate as well as the final product were analyzed by X-ray diffraction measurement and the crystallite dimensions evaluated by using the Scherrer's formula. The iron metal/lithium fluoride mixture was used as a conversion material and its electrochemical properties evaluated by galvanostatic charge discharge cycles, impedance spectroscopy and galvanostatic intermittent titration technique. As the conversion material is in its reduced state it can be coupled with a carbonaceous negative electrode to build a lithium ion battery, opening new perspectives for using conversion materials in lithium ion batteries technology.

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1. Introduction

The discovery of the intercalation materials allowed the development and large scale commercialization of lithium ion batteries. The intercalation materials are oxide or other anions of transition metals characterized by the presence of interstitial sites in which the lithium ions can be hosted with minimal structural changes. The main advantage of these materials is the great reversibility and long cycle life, while the main drawback is the low specific capacity related to the intercalation reaction. In fact, to avoid major structural modification, the number of exchanged electrons has to be limited to 0.5–1.0 per mole of transition metal. One route for achieving a larger specific capacity is to utilize all possible oxidation states of the metal through a conversion reaction in which more than one electron can be transferred per transition metal. Conversion reaction is usually applied to define the reaction of a binary transition metal compound, M_aX_b (M = transition metal, X = O, S, F, P, N, ...) with lithium to yield metallic nano-particles embedded in a matrix of Li_nX that can be generalized as:



where M is the transition metal, X is the anion, and n is the formal oxidation state of X .

Based on this concept, many transition metal compounds that had been disregarded as electrode materials, as they do not have any vacant sites in their structure to allow lithium insertion, can be reconsidered as extremely high capacity conversion materials. The main advantage of the conversion reaction is the large increase in electrochemical capacity. In fact, in particular cases, the reaction can bring to the full reduction of the transition metal to its metallic state, delivering remarkably high capacity values. The main drawback is that the large capacity values are achieved at the expense of major structural changes. The structural changes are responsible of severe capacity fading and consequently poor cyclability of the electrode.

Tarascon's group first demonstrated that transition metal oxides such as Co_3O_4 , CoO , NiO , and FeO , can exhibit specific capacities as high as 600–1000 $mAh\ g^{-1}$ along with good cycling properties [1–3]. In addition to the oxides, other conversion compounds of interest include hydrides, sulphides, nitrides, and fluorides [4–9]. However, due to their low conversion voltage which is between 0.5 and 1.0 V, most of these materials are only suitable for use as negative electrodes. The main exception is for fluorides, which react at remarkably high values (close to 3.0 V), enabling their use as positive electrode materials and transition metal fluorides have been recently investigated as potential cathode materials [10–13]. Nanocomposites of carbon and metal fluorides such as FeF_2 , FeF_3 , and BiF_3 have been recently used as high energy cathode active material in lithium batteries, revealing a high conversion potential and good cycling properties [14–16]. Recent studies have shown that

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the electrochemical lithiation of FeF_3 includes an insertion step and multiple phase transitions, followed by a conversion process [17,18]. Nevertheless, problems with poor kinetics, cycle life, and reversibility are only some of the challenges that hinder the potential commercialization of these electrodes [19]. Despite decades of efforts and intense recent interest, the basic mechanisms of the conversion reaction are not well understood [20,21]. The good cycling characteristics of the systems exhibiting high reversibility, such as metal oxides and fluorides, are attributed to the in situ formation of fine metallic nanoparticles embedded in an insulating matrix (e.g., Li_2O or LiF). This configuration allows for rapid mass transport since the diffusion distances remain short during the redox process. However, the insulating nature of metal fluorides has limited their electrochemical properties for a long time; for that reason a considerable amount of attention has been devoted by Badway et al. [22–24] to tailor their nanostructures to overcome poor electronic conductivity. However, it is interesting to note that conversion electrodes prepared with the metal in the reduced state (e.g., $\text{LiF} + \text{M}$), by mechanically mixing metallic nanoparticles with the lithium fluoride, are electrochemically inactive (aside from a small amount of capacity in grain boundaries at low voltages) [25]. Only few examples are known reporting the electrochemical activity of conversion materials in their reduced state [26–28]. The impossibility to use the conversion materials in the discharge state strongly limits the practical applications of these compounds in lithium ion technology since they have to be coupled with a pre-lithiated anode. To overcome this problem Amatucci et al. [29] introduced the use of a solid state Li_3N route to achieve the lithiation and mechanoreduction of metal fluoride based nanocomposites. The resulting prelithiation was found to be effective with the formation of $x\text{LiF}:\text{Me}$ structures of very fine nanodimensions analogous to what is found by electrochemical lithiation. In this paper we are proposing a similar way to obtain nanosized metal particle embedded in a matrix of lithium fluoride to be used as a positive electrode in lithium-ion battery. The transition metal oxide is transformed into the metal by solid state reduction with lithium hydride. The lithium oxide obtained as sub product is converted into lithium fluoride by solid state reaction with ammonium fluoride. In this work the proposed method is applied to iron(III) oxide. The iron oxide is reduced to form iron metal and lithium oxide and this latter is transformed into lithium fluoride. The materials were characterized by XRD measurement and SEM. The iron metal/lithium fluoride mixture was used to prepare a composite electrode and its electrochemical properties were tested in lithium batteries.

2. Experimental

Synthesis of iron metal/lithium oxide. Iron(III) oxide (Aldrich, 99.98%) and lithium hydride (Aldrich, 95%) were used as received. The lithium hydride (0.5 g, 60 mm) was ground in a mortar. The iron oxide (1.57 g, 10 mm, Fe/Li atomic ratio 1:3) was added in small portions and the mixture was well grinded after each addition. The powder was transferred into a ceramic crucible which was placed inside a quartz tube. The oxygen within the tube was removed by flowing a nitrogen/hydrogen mixture. After few minutes the flow was slowed down to 100 ml min^{-1} and the tube was placed in an oven preheated at 700°C . After 1 h the tube was extracted from the oven and cooled. When the temperature reached the ambient temperature, the crucible was removed from the tube and the solid weighed to evaluate the reaction yield.

Synthesis of iron metal/lithium fluoride. The ammonium fluoride (Aldrich, 98% ACS reagent) was used as received. The ammonium fluoride (2.15 g, 57 mm) was ground in a mortar. The iron metal/lithium oxide mixture (1.8 g, 19 mm of Fe, Fe/F atomic ratio 1:3) was added and mixed. The powder was transferred into a ceramic crucible which was placed inside the quartz tube.

The oxygen within the tube was removed by flowing a nitrogen/hydrogen mixture. After few minutes the flow was slowed down to 100 ml min^{-1} and the tube was placed in an oven preheated at 500°C . After 1 h the tube was extracted from the oven and cooled to room temperature. The crucible was removed from the tube and the solid weighed to evaluate the reaction yield.

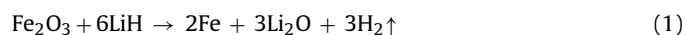
XRD characterization. Phase identification was performed by XRD analysis using a Rigaku MiniFlex diffractometer with $\text{CuK}\alpha$ radiation. The Scherrer's formula was used to evaluate the crystallite dimensions.

Scanning electron microscopy. The morphology of the materials was evaluated by a AURIGA, CrossBeam Workstation dual column Focused Ion Beam – Secondary Electron Microscope (SEM), equipped with an Energy Dispersive X-ray Spectrometer (EDS) to analyze the atomic composition of the samples.

Electrochemical characterization. The active material and the carbon (Super P, MMM Carbon) were weighted in a 8.5:1 ratio and mixed in a mortar. 5 wt.% Teflon, used as a binder, was added and the resulting blend was mixed in the mortar for obtaining a plastic like material. Composite cathode tapes were made by roll milling the plastic material to reduce the thickness to about $90\text{--}100 \mu\text{m}$. The final compositions of the cathode tape was: active material 85 wt.%, carbon 10 wt.% Teflon 5 wt.%. The electrodes were punched in form of discs with a diameter of 12 mm. The electrode weights ranged from 25.6 to 28.3 mg corresponding to an active material mass loading of 21.8 and 24.0 mg cm^{-2} . The electrodes were assembled in sealed cells formed by a polypropylene T-type pipe connector with cylindrical stainless steel (SS316) current collectors. A lithium foil was used both as anode and reference electrode and a glass fiber as a separator. The cells were filled with ethylene carbonate/diethyl carbonate 1:1 LiPF_6 1 M electrolyte solution (Merck, battery grade). The cycling tests were carried out automatically by means of a battery cycler (Maccor 4000). To assess the charge/discharge capability, the electrodes were galvanostatically cycled between 1.0 and 4.5 V at C/30 rate. For the Galvanostatic Intermittent Titration Technique (GITT) measurements, the cell was galvanostatically cycled at C/60 rate for 15 min followed by a rest period at open circuit voltage of 60 min. Electrochemical Impedance Spectroscopy (EIS) was employed to characterize the composite cathode, using a frequency response analyzer (FRA Solartron mod. 1260) in a frequency range of 50 kHz to 100 mHz with a 10 mV amplitude. Ten points per decade change in frequency were recorded. Composite cathode preparation, cell assembly, test and storage were performed in the dry room (R.H. <0.1% at 20°C).

3. Results and discussion

XRD characterization. The lithium hydride and the iron(III) oxide were mixed in a 6:1 stoichiometric ratio and heated at 700°C to reduce the iron oxide as described in the following equation:



The diffraction pattern of the so obtained material is shown in Fig. 1. The material is identified as a mixture of metallic iron, card no. 6-696, lithium oxide (Li_2O), card no. 12-254 and Li_5FeO_4 , card no. 24-623. The presence of metallic iron and lithium oxide confirms the occurrence of the reaction (1). The Li_5FeO_4 can be the result of the reaction of the lithium oxide, produced by the reaction (1) with un-reacted iron oxide as described in Eq. (2).



The peaks are short and broad, indicating that the crystal structure has a short range coherence. The Scherrer's formula was used to evaluate the crystal size of the crystallite: $d = k\lambda/B \cos \theta$ where d is the size of the crystallites, k is a constant that depends on the

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