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Short communication

On the growth of nanostructured iron hydroxy-fluorides for Li-ion batteries

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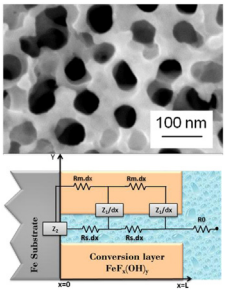
HIGHLIGHTS

- Electrochemically grown nano-structured hydroxyl fluorides.
- Impedance-based methodology for in-situ characterization.
- Conversion reaction for material preparation and energy recovering.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium ion battery applications such as transportation or renewable energies require cost effective, environmentally friendly and high capacity materials. Conversion reaction with iron based materials at positive electrode is a promising route to reach this target.

In this work, iron hydroxyl-fluoride conversion coatings are prepared by an electrochemical way. The structure of the produced coatings is nano-porous with a pore diameter of about 75 nm. An impedance-based methodology is proposed for in-situ characterisation of the conversion coatings during the preparation procedure and enables to optimize the process parameters to get a 3D nano-porous structure. The cycling tests performed in coin-cell versus lithium reference electrode show a promising cycling behaviour for the prepared nano-porous coatings.

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1. Introduction

In order to improve the technical and economical performance of energy storage, most of the research in this field is focused on the development of new electrode materials for batteries. Particularly, lithium-ion batteries have important capacity limitations due to the electrode materials mainly at the positive electrode. An alternative proposed to increase the capacity could be the use of nanostructured materials, such as nanostructured iron fluorides for positive electrode. These materials enable to obtain high specific capacity [1,2] on the order of 700 mAh g^{-1}.

Most papers dedicated to the study of electrode materials are based on the use of powders whose characterization is done a posteriori, on the compacted sample, by X-ray diffraction, XRD, and Scanning electron Microscopy, SEM, examination and composite electrodes (including the powders mixed with a binder and a conducting agent spread on a metallic sheet) are made to evaluate the electrochemical properties as battery material. Nevertheless, the approach reported in the present paper is

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different because conversion layers constituting the active material of the electrode are directly developed on the electrode, which makes it bi-functional: holder of the active material and current collector.

This new approach requires a tool capable of providing information on the development of the layer during the growth period. The Electrochemical Impedance Spectroscopy, EIS, was chosen for this purpose and first results are the subject of this communication.

2. Experimental

2.1. Preparation and in-situ characterisation of the conversion coatings

The substrate material used was an iron strip (Goodfellow, 99.99%) constituting the working electrode of an electrochemical cell with a platinum mesh as counter electrode and a Pt wire as pseudo reference electrode. The nominal active surface areas of the working electrodes were between 0.28 cm^2 and 2.0 cm^2, depending on the further test requirements.

The formation of conversion coatings was carried out by anodizing in a range of applied potential (two electrodes) between 25 V and 150 V, for up to 15 min. The best results in terms of porosity were obtained at 50 V for 15 min and are the object of the present report. The electrolyte solutions used were based on ethylene glycol (ETG) and water [3] containing NH_4F.

The expected electrochemical processes are:

a) At the anode (the iron working electrode):
- Formation of the conversion layer through the process

$$Fe + xF^- \rightarrow FeF_x^{(3-x)+} + 3e^-$$

- Water oxidation through the process

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

b) At the cathode (the platinum counter electrode):
- Reduction of the ammonium cations through the process

$$NH_4^+ + e^- \rightarrow NH_3 + \frac{1}{2}H_2$$

- Water reduction through the process

$$2H_2O + 2e^- \rightarrow 2OH^- + O_2$$

Thus, a fluoride-rich conversion layer will be produced together with a side reaction which is water electrolysis.

The characterization of the coatings by EIS was done in the same solution after interrupting the electrolysis current and stabilization of the potential. The impedance was then determined at the open circuit potential using Pt pseudo reference, between 10 kHz and 10 mHz, taking seven points per decade and using an AC amplitude of 10 mV rms. The measures were managed by a system AUTOLAB (Ecochemie®) based on a potentiostat PGSTAT 30.

2.2. Cycling and ex-situ characterisation of the conversion coatings

Square shaped samples of 1 cm^2 were dried at 80 °C under vacuum for 2 h. A 2035-size coin cell was made to examine the electrochemical properties of the layer. The cell was assembled in a glove box filled with dry air. Lithium foils (Chemetall Foote Corp.) and polypropylene films were used as counter electrode and separator, respectively. The electrolyte used was 1 M $LiPF_6$ dissolved in ethylene carbonate, EC/diethyl carbonate, DEC, solution (1/1, v/v). The coin cells were galvanostatically cycled using a 30 μA cm^{-2} current density and a voltage window of 1.5 V–4 V.

The morphology of the fluoride layer was investigated by scanning electron microscopy (FEG-SEM Zeiss Supra 55) before cycling and after 200 charge–discharge cycles. To do so, the coin cell was stopped after 200 cycles at 4 V in the charged state. Then, it was dis-assembled in the glove-box, rinsed in a dimethyl carbonate (DMC) solution and dried in the glove box before SEM observation.

3. Results and discussion

3.1. Preparation and in-situ characterisation of the conversion coatings

The general trend of the chronoamperograms obtained during the electrolysis is depicted in Fig. 1A. The presence of three domains is easily distinguished: Germination (0–30 s), growth (30–120 s) and a pseudo steady state from 120 s.

The exponential decay of the current observed in Fig. 1A can be attributed to the fast formation of a passive layer, as evidenced by the high impedance values obtained, as shown in Fig. 1B for 5 s and 20 s of electrolysis. After that initial short period, the current

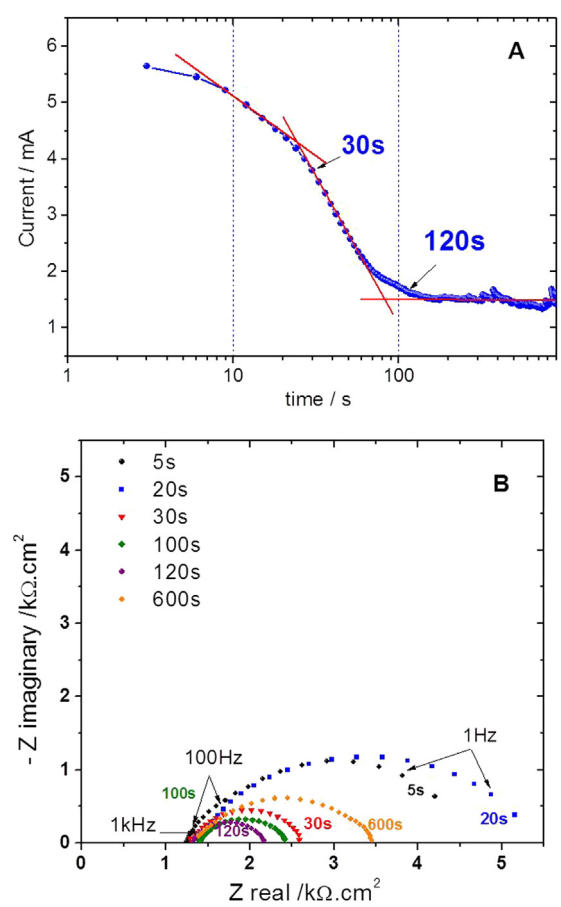

Fig. 1. A) Chronoamperogram obtained during the synthesis of a conversion layer on a 0.20 cm^2 Fe electrode at 50 V in ETG solution containing NH_4 F and H_2O. B) Nyquist impedance diagrams recorded at selected times during the electrolysis.

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