Electrochemical Properties of Lithium Iron Oxides Prepared by Low Temperature Synthesis

L. Bordet-Le Guennea, P. Deniardb, A. Lecerfc, P. Biensanc, C. Siretd, L. Fournéd and R. Brec a

a I.M.N., Laboratoire de Chimie des Solides
2 rue de la Houssinière, B.P. 32229, 44322 Nantes cedex 3, France
b I.N.S.A., Laboratoire de Chimie des Solides
20 av. des Buttes de Coësmes, 35043 Rennes cedex, France
c SAFT, route de Nozay, 91460 Marcoussis, France
d I.C.M.C.B., 162 av. du Dr. Schweitzer, 33608 PESSAC cedex, France

Abstract. Two lithium iron oxides r-Li0.8H0.2FeO2 (ramsdellite-type) and o-Li0.7H0.3FeO2 (orthorhombic structure) have been synthesised by an ion exchange reaction between respectively α-FeOOH and γ-FeOOH, and C2H5OLi at 170 °C and 140 °C. The reaction products were characterised through elemental analyses, infrared spectroscopy, density measurements and X-ray diffraction. The refinement of the powder XRD patterns of r-Li0.8H0.2FeO2 and o-Li0.7H0.3FeO2 has been performed by the Rietveld method and the results show that the products are isostructural to their precursors. Electrochemical measurements of Li1-xHxFeO2/Li have been made in lithium cells in the 1.5 - 5 V range. Their elemental analyses and the study of X-ray diffraction results and Mössbauer spectroscopy measurements show the instability of Fe4+ in the electrochemically produced species in the electrochemical cell, and therefore the difficulty of cycling on the couple FeIV/FeIII.

1. Introduction
A number of materials have been synthesised and evaluated for use as the cathode active material in room temperature lithium secondary batteries. Among them, a series of LiMO2 (M = Co, Ni, Mn, Fe) cathodes have been extensively studied. LiFeO2 is a prospective candidate from the viewpoints of environmental friendliness and cost. Although LiFeO2 has several polymorphs [1-9], only two varieties, the orthorhombic phase o-LiFeO2 and the ramsdellite phase r-LiFeO2, are reported to show electrochemical rechargeability in a lithium cell [10-20]. However, their cycling properties are good only in the voltage range 1.5 to 3V [16-18]. These two lithium iron oxides have the same structure as some cathodic materials with good electrochemical properties (MnO2 ramsdellite and o-LiMnO2 orthorhombic). Consequently, we found interesting to study these two polymorphs to understand their structural and electrochemical behaviours in the high potential range (E > 3 Volts).

2. Experimental Section
2.1. Synthesis. r-Li0.8H0.2FeO2 and o-Li0.7H0.3FeO2 were prepared by reaction of suspension in anhydrous ethanol of α-FeOOH and γ-FeOOH with lithium ethoxide, in autoclave between 170 °C and 140 °C, respectively. The expected topotactic reactions are:

\[ \alpha\text{-FeOOH} + C_2H_5OLi \rightarrow r\text{-LiFeO}_2 + C_2H_5OH \]

170 °C - 15h

\[ \gamma\text{-FeOOH} + C_2H_5OLi \rightarrow \text{LiFeO}_2 + C_2H_5OH \]

140 °C - 15h

The mixture corresponded to a ratio Li : Fe = 1 : 1. The powders obtained after reaction were filtered and washed with ethanol and dried under vacuum at 200 °C for the ramsdellite type and 100 °C for the orthorhombic form.
The amounts of Li and Fe in the reaction products were analysed by inductively coupled plasma atomic emission spectroscopy, and some impurities as Li₂CO₃ detected by infrared measurements. Due to an incomplete substitution of Li⁺ for H⁺ in FeOOH some protons remain in the structure.

2.2. X-Ray Diffraction. The X-ray diffraction powder patterns have been recorded on a SIEMENS D5000 diffractometer, without monochromator, and with Ni filter (Cu-Kα₁ = 1.540598 Å and Cu-Kα₂ = 1.544390 Å) in a Bragg-Brentano geometry.

2.3. Cell Preparation and Electrochemical measurements. Electrochemical charges and discharges of Li₁ₓHₓFeO₂/Li systems have been made in electrochemical cells of the button type that were mounted in an argon filled dry box with water and oxygen contents lower than 1 ppm. The cathodic mixture was prepared manually with the following weight compositions: 80 % of Li₁ₓHₓFeO₂, 7.5 % graphite, 7.5 % soot and 5 % Algoflon (aqueous emulsion of Teflon). The preparation of the disks of cathodic material (Ø = 0.75 cm) was described elsewhere [21]. The anode was a disk of lithium metal (Ø = 0.75 cm). The electrolyte was constituted of a mixture of propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMC) in the volume proportions 1 : 1 : 3 respectively and of LiPF₆ 1M for the lithium salt dissolved in the solvent mixture. The battery testing machine MACPILE was used to perform potentiostatic experiments (5 mV/h) between 1.5 and 5 V.

3. Results and Discussion

3.1. Characterisation and X-Ray Structure Refinement. The results of elemental analysis and density measurements completed by infrared spectroscopy measurements and thermal analyses allowed the determination of the compositions: r-Li₀.₅H₀.₂FeO₂ and o-Li₀.₅H₀.₃FeO₂. Refinements of the XRD powder patterns of r-Li₀.₅H₀.₂FeO₂ and o-Li₀.₅H₀.₃FeO₂ were performed by the Rietveld method using the program FULLPROF (Figs. 1 and 3). Refined cell constants and additional relevant data of the refinement of the structures are given in Tables 1-4.

For the r-Li₀.₅H₀.₂FeO₂ phase, only the cell parameters were given by Y. Sakurai et al. [17]. The structure is similar to that of the precursor α-FeOOH. It is an association by pairs of [FeO₆] octahedra layers to give tunnels (1*2) forming chevrons (Fig. 2).