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Lithium-induced conversion reaction in wüstite $Fe_{1-x}O$ studied by ^{57}Fe Mössbauer spectroscopy

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ABSTRACT

$Fe_{1-x}O$ wüstite as negative electrode material for Li-ion batteries has been studied. The aim of this work is to get a better understanding of the insertion mechanism involved during reduction/oxidation processes. Electrochemical tests have been done in Swagelock™ cells and shown a high specific capacity of 800 A h/kg for the first discharge. X-ray diffraction and ^{57}Fe Mössbauer spectroscopy provide us valuable information on both local and long range order. Hence, Li reaction with wüstite induces formation of highly divided metallic iron (α-Fe and nano-Fe) and Li_2O with a small amount of Fe_2O_3 occurring in a diffusion layer at the surface of the primary particles. Based on the X-ray and Mössbauer spectroscopic analyses, a core–shell model is proposed in order to explain the irreversible capacity of about 1 Li observed at the first cycle. It involves cation diffusion induced by lithium acting as an 'electronic pressure'.

1. Introduction

Anodic materials having a discharge potential of 1V/Li are chosen among the metallic oxides [1,2]. Iron oxides are inexpensive and present low environmental impact for lithium battery applications [3,4]. Previous works have shown the interest of such iron oxides as electrochemically active material [5,6]. The mechanism is generally based upon the redox couple Fe^{3+}/Fe^{2+} working at approximately 0.5 V compared to lithium [7,8]. Wüstite is a non-stoichiometric compound with formulas $Fe_{1-x}O$, with $0.83 < x < 0.96$ [9]. It has the rocksalt structure with a cell parameter of 4.307 Å [10]. In the structure some Schottky defects occur because of the presence of two oxidation states Fe^{II} and Fe^{III}, occupying the octahedral sites of the structure. Fe^{II} is rather easy to oxidize to Fe^{III} and can explain the wide range of composition. In order to get a better understanding of electrochemical Li reaction mechanism into $Fe_{1-x}O$, the present work deals with ^{57}Fe Mössbauer spectroscopy, X-ray diffraction and electrochemical tests. Coupling these experimental techniques allows us to get deeper insight into the mechanism ruling lithium reaction processes in the $Fe_{1-x}O$ wüstite phase.

From X-ray diffraction, previous work has shown a correlation between amount of vacancies and cell parameters [11]. From ^{57}Fe Mössbauer spectroscopy the relative contribution of Fe^{II} and Fe^{III} to the spectrum can be determined [12,13]. Hence comparison between the amount of vacancies from X-ray diffraction and Mössbauer spectroscopy can be done. This nuclear technique gives local information at the atomic scale and is very sensitive of the neighborhood in terms of charge of ions and vacancy effects [14,15].

The electrochemical mechanism shows that a part of Li (~44%) is involved in the reduction of FeO into metallic Fe^0 accompanied with small amount of nanosized Fe_2O_3 and a last part of Li (~56%) is consumed to form a SEI in the first discharge. This last part seems to be responsible for the irreversible capacity in this conversion reaction. The reversible process is based on a reversible reaction: $Fe^{II}O + 2Li \leftrightarrow Fe^0 + Li_2O$.

2. Experimental

2.1. Synthesis conditions

Wüstite $Fe_{1-x}O$ has been prepared from powdered hematite α-Fe_2O_3 by specific heat treatment [9]. Hematite has been ground in

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an agate mortar and then the fine powder has been put into a porcelain crucible. The crucible is then placed in the quartz tube of the oven at 800 °C under H_2 atmosphere used as reducing agent [16]. Since $Fe_{1-x}O$ is metastable [17,18] and decomposes below 570 °C to magnetite Fe_3O_4 and metallic Fe at ambient pressure and temperature, the crucible has been quenched outside by cooling with pulsed air.

2.2. X-ray diffraction

X-ray diffraction (XRD) patterns were collected on a conventional Philips $\theta-2\theta$ diffractometer with Cu-K_α radiation (1.5418 Å) and a nickel filter in order to characterize the compounds before and after insertion of lithium. For electrochemically-inserted phase, the recording was made under vacuum in order to avoid undesirable reactions with air.

2.3. ^{57}Fe Mössbauer spectroscopy

^{57}Fe Mössbauer spectra were recorded at room temperature (RT) using transmission geometry in the constant acceleration mode with a spectrometer based on electronic devices delivered by EG&G and WissEl. The absorbers contained 1–2 mg of ^{57}Fe per cm^2 were prepared inside the glove box, and sealed with parafilm to avoid contact with air. The velocity scale was calibrated using the 2 inner lines (*see below*) of the magnetic sextet of a high purity iron foil absorber as a standard, using ^{57}Co (Rh) as the source. The spectra were fitted using a Lorentzian approximation by least-squares method implemented in our GM5SIT program [19,20]. The quality of the fit was controlled by the conventional χ^2 test. Isomer shift (IS) values are given relative to the centre of the α-Fe (10 μm foil) spectrum recorded at room temperature. The shape of a Mössbauer spectrum of a paramagnetic compound is generally determined by a doublet, characterized by the quadrupole splitting (QS) separating more or less the 2 Lorentzian lines and their mean position, the isomer shift (IS). The intensity of the absorption (A) is ruled by the number of sites (N) and the Lamb–Mössbauer factor (f) through $A = N.f$.

In the case of magnetic contribution, the spectrum is split into 6 Lorentzian lines with a relative intensity as 3:2:1:1:2:3. Mössbauer spectra of bulk α-Fe or Fe_2O_3 present such a magnetic sextet. The sextet of α-Fe used for velocity calibration is composed of two lines located at $IS_{1,6} = \pm 5.33$ mm/s with relative intensities of 3, two other lines at $IS_{2,5} = \pm 3.02$ mm/s with relative intensities of 2. The inner lines of the sextet have relative intensities of 1. Since we present in the following Mössbauer spectra recorded in a small velocity range [±2.4 mm/s] to favor details in the Fe^{III}/Fe^{II} velocity scale, we can only detect the two inner lines $IS_{3,4} = \pm 0.84$ mm/s. For convenience, we choose to fit these two lines with an equivalent doublet with IS ~0 mm/s and QS ~1.68 mm/s. After convergence of the fitting procedure, we have to correct the total absorption of our sample. We have multiplied by 6 the relative contribution of this doublet to get the real contribution of metallic α-Fe in the mixture. The same procedure will be used with a magnetic contribution of Fe_2O_3. Then, all contributions are corrected to obtain the relative amount of the species.

Concerning the non-stoichiometric wüstite phase, $Fe_{1-x}O$ will be written taking into account the amount of vacancies, $\boldsymbol{x}$, as $Fe^{II}_{1-3x}Fe^{III}_{2x}\square_{x}O$. This quantity can be roughly estimated from the relative contributions A_{II} and A_{III} from the Mössbauer spectroscopic data by:

$$x = \frac{1}{3 + 2A_{II}/A_{III}}$$

It is thoroughly admitted in the Mössbauer community that vacancies or 'guest' ions can be detected in the vicinity of the probed ion or atom (^{57}Fe) from the quadrupole splitting distribution as shown by Womes et al. [21]. The presence of both Fe^{III} and vacancies in the vicinity of probed Fe^{II} may change the electric field gradient (EFG) and therefore the measured quadrupole splitting (QS). The quadrupole splitting reflects the ferrous quadrupole interaction in the paramagnetic state and is related to the elements of the diagonalized electric field gradient tensor that can be estimated for ionic compounds from point charge model calculations [22].

Assuming a random distribution [23,24] of both vacancies and cations in the wüstite structure, the probability of a probed Fe^{II} to have n Fe^{III} ions, m vacancies at a concentration x and 12-m-n Fe^{II} located in the 12 neighboring sites of the first coordination shell of $Fe_{1-x}O$ is given by:

$$p_{n,m}(x) = \frac{12!}{n!m!(12-n-m)!}2x^{n+m}(1-3x)^{12-n-m}$$

Since the solid solution domain is not very extended for $Fe_{1-x}O$ ($x < 0.1$), we think that the main contributions are due to electric charge as often observed for ionic compounds [25]. The most probable configurations will be grouped according to the values of n and m. For instance a Fe^{II} surrounded by $n = 1$ Fe^{III} and $m = 0$, 1 or 2 vacancies will give an intensity proportional to $P_1 = P_{1,0} + P_{1,1} + P_{1,2}$ if we neglect the cases where $m > 2$ since $x < 0.1$. Hence 3 main contributions $P_n = P_{n,0} + P_{n,1} + P_{n,2}$ ($n = 0, 1$ or 2) will be the most probable and expected configurations. In this case we believe that the measured quadrupole splitting will be n-dependant.

The intensity of the absorption of a given phase depends on its recoil-free factor f (named the Lamb–Mössbauer factor [26,27]). The factor f depends on the Debye temperature, θ_D, which decreases with decreasing particle size [28]. It is worth noticing that dispersed Fe nanoparticles not bound to a rigid matrix show a large decrease in the apparent Debye temperature. Indeed the Debye temperature has been estimated to 388 ± 20 K for bulk α-Fe. This value decreases to 344 ± 16 K and 259 ± 18 K for particles of 2.5 nm and 1.5 nm in size, respectively [29]. For wüstite it has been estimated to $\theta_D = 417$ K [30]. Knowing the Debye temperature of a given material, the Lamb–Mössbauer factor, which depends on the temperature and on the recoil energy ($E_R = 1.956$ meV for ^{57}Fe), can be estimated through:

$$\ln f_{LM}(T) = -\frac{6E_R.T}{k\vartheta_D^2}$$

In the discussion species fraction, $\boldsymbol{n_i}$, will be estimated assuming a given $\boldsymbol{f_i}$ factor from the relative intensity $\boldsymbol{A_i}$ of the Mössbauer absorption using $\boldsymbol{n_i = A_i/f_i}$.

2.4. Electrochemical tests

The cells consisted of lithium disks (anode) and pellets of wüstite $Fe_{1-x}O$ samples (diameter = 7 mm, thickness ~ 0.3 mm) (cathode), and we used 2 Whatman separators wetted by $LiPF_6$ (1 M) electrolyte in PC-EC-3DMC. Charge/discharge curves were carried out galvanostatically by means of a MacPile™ system operating at a current density of 10 A/kg (C/15 rate) between 3 and 0 V vs. Li. Some cells have been stopped at a given depth of discharge or charge, disassembled in a glove box to avoid air and/or moisture contamination.