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TG AND DSC STUDIES OF LITHIUM INSERTION IN $LiFe_5O_8$

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ABSTRACT

The chemical lithiation of $LiFe_5O_8$ with n-butyl-lithium leads to the formation of $Li_{1+x}Fe_5O_8$, which is accompanied by unreacted α-$LiFe_5O_8$ and Li_2CO_3. The DSC traces of this material in air atmosphere show an exothermal effect at ca. 320°C which is associated with a weight increase, due to the decomposition of the lithiated phase to $LiFe_5O_8$ and Li_2O. A complex endotherm of low intensity and a weight loss effect are found at 430-550°C. These are interpreted in terms of the reaction of $LiFe_5O_8$ with Li_2CO_3 to give α-$LiFeO_2$. The thermal treatment of the **material** in vacuum **leads to the reaction** between $LiFe_5O_8$ and $Li_{1+x}Fe_5O_8$ to give a rock-salt phase with a=8.362 Å.

INTRODUCTION

Recently, the chemical and electrochemical lithiation of several phases in the Li-Fe-O system has been the subject of extensive research work. De Picciotto and Thackeray [1] inserted lithium into the spinel $LiFe_5O_8$ (S.G. $P4_132$). This process yielded a multiphase product with overall composition $Li_{2.8}Fe_5O_8$. In the lithiated phase, these authors assumed a displacement of tetrahedral ferric ions into vacant octahedral sites, without losing the long-range order of lithium and iron ions on the B-sites. Electrochemical lithiation was used to obtain a rock-salt phase with random distribution of cations on the B-sites. On the contrary, Chen at al. [2] found the occurrence of $Li_5Fe_5O_8$ (S.G. Fm3m) as the product of lithium insertion in the spinel $LiFe_5O_8$. In this phase, the inserted lithium ions were assumed to be distributed either on octahedral and tetrahedral sites. The oxidative delithiation of $Li_5Fe_5O_8$ produced the rock-salt phase $Li_3Fe_5O_8$.

The various structural possibilities found in these studies and the fact that these products are not easily prepared as single phases may condition the thermal evolution of chemically lithiated α-$LiFe_5O_8$. In this work the

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preparation and the study of TG and DSC data of these products are carried out.

EXPERIMENTAL

A polycrystalline α-$LiFe_5O_8$ sample was prepared by the ceramic method from stoichiometric mixtures of Fe_2O_3 and Li_2CO_3. The X-ray diffractograms of this sample (Fig. 1f) showed a high-purity phase. This material was chemically lithiated by using a 1.6 M solution of n-butyl-lithium in hexane. The reaction was carried out under N_2 atmosphere at 37°C for 4 days. Total Li and Fe contents were determined by atomic absorption spectrometry.

DSC traces were obtained with a Mettler TA 3000 apparatus under static air atmosphere. TG traces in vacuum and air atmosphere were carried out in a Stanton STA 781 apparatus. X-ray diffraction patterns were obtained with a Siemens D500 diffractometer with CuK_α radiation, monochromated by a graphite crystal.

RESULTS AND DISCUSSION

After 4 days of chemical lithiation, the sample changed from brownish-red to black and lost its magnetic properties with respect to its interaction with the bar of a magnetic stirrer. The X-ray diffraction pattern of this product (Fig. 1a) shows the presence of unreacted α-$LiFe_5O_8$ (a=8.332 Å) and a lithiated phase $Li_{1+x}Fe_5O_8$ (a=8.401 Å). If the observed intensity ratio I_{400}/I_{440} of the lithiated phase (1.5) is compared with that of α-$LiFe_5O_8$ (0.7), a diffusion process of Fe(III) ions from tetrahedral 8a to octahedral 16c sites can be detected simultaneously to Li insertion in the spinel structure.

The chemical composition of the global product as determined by atomic absorption spectrometry showed a Li/Fe ratio of 0.86. A lithiated sample with higher Li/Fe ratio could not be prepared. Thus, from 4 to 10 days of treatment with n-butyl-lithium, no significant increase in the ratio was observed.

Fig. 2a shows the DSC trace of the lithiated product recorded under static air atmosphere. At ca. 100°C, an endothermal effect is found which is accompanied by a weight loss effect in the TG traces (Fig. 2b). This effect can be interpreted as the release of adsorbed water and does not affect the phase composition of the product. At 320°C, a sharp exothermic process takes place, simultaneously to a weight increase. This effect may be ascribed to the oxidative decomposition of the lithiated phase, giving place to the progressive oxidation of Fe(II) into Fe(III). This process is observed in the X-ray

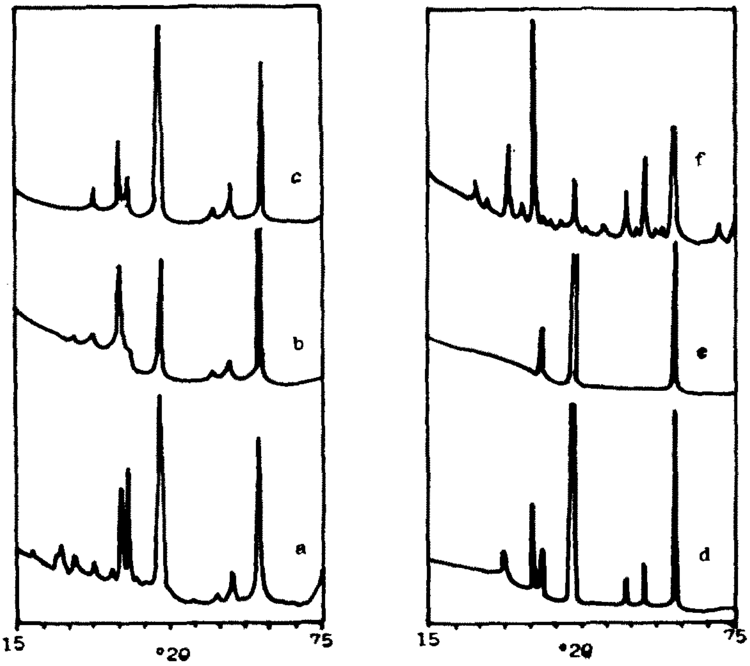

Fig. 1. X-ray diffractograms of (a) lithiated $LiFe_5O_8$, (b,c,d) lithiated $LiFe_5O_8$ heated in air at 340, 550 and 750°C, (e) heated in vacuum at 750°C, (f) original α-$LiFe_5O_8$. (°) $Li_xFe_5O_8$, (+) α-$LiFe_5O_8$, (#) α-$LiFeO_2$.

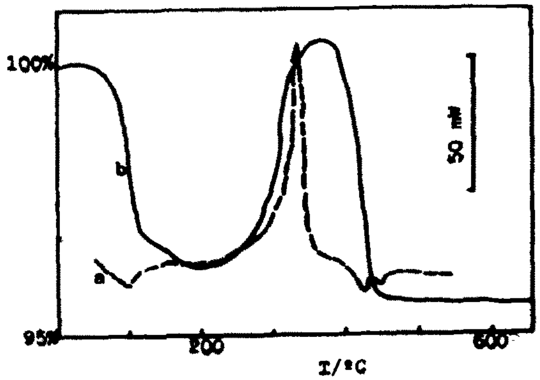

Fig. 2. DSC (a) and TG (b) traces of the lithiated $LiFe_5O_8$ sample.

diffractograms by the loss of the diffraction lines corresponding to the lithiated phase (Fig. 1b). The quantitative evaluation of TG data yielded a Fe(II)/Fe(total) = 0.474. After the complete decomposition (Fig. 1 c and d), the ferrite α-$LiFeO_2$ (a=4.158 Å) is detected. The endothermal effect found in the DSC trace at 400-450°C (Fig. 2a), which is accompanied by weight loss effects can be identified as the thermal decomposition of contaminant Li_2CO_3 as found in other systems [3]. This reaction may account for a higher Li_2O content that may react with $LiFe_5O_8$ to give additional $LiFeO_2$. This process is shown in the X-ray diffractogram of Fig. 2d by the increase in the 111, 200 and 222 line intensities.

From the observed weigth loss, the value of the Li_2CO_3 content is calculated to be 7.6 %. These results imply a stoichiometry of the lithiated product $Li_{3.3}Fe_5O_8$ if the Fe/O ratio is assumed to be 5/8. As these calculations did not take into account the presence of unreacted $LiFe_5O_8$ in the sample, the Li/Fe ratio expected for the lithiated phase is probably higher than 3.3/5. In any case, these results **demonstrate the Li occupancy of tetrahedral sites, probably** 8a, which are in contact with the octahedral 16c sites that are progressively filled during Li insertion. This process corresponds with the results of Chen et al. [2], although the product is not rock-salt structure and maintains the ordering of the B-sites of the spinel structure. Additionally, these authors found a single-phase product $Li_5Fe_5O_8$ without unreacted solids. The difference of reactivity may be related to a higher particle size of $LiFe_5O_8$ in our case.

On the other hand, a notorious change in thermal behaviour is found when the lithiated material is heated in vacuum (Fig. 1e). The product obtained at 750°C shows a diffractogram which is representative of a rock-salt structure with a=4.181 Å. This value is intermediate between α-$LiFeO_2$ (4.158 Å) and $Li_5Fe_5O_8$ (4.197 Å). The diffraction lines corresponding to the ordering of the B-sites in the spinel-derived structures of $Li_{1+x}Fe_5O_8$ and unreacted $LiFe_5O_8$ disappear, indicating the development of a statistical distribution of cations in the octahedral sites. This, however may not discard a fractional occupancy of the tetrahedral 8a sites by Li^+ ions, which are difficult to discern from X-ray diffraction data. This process is similar to that found by De Picciotto and Thackeray [1] in thermally and electrochemically delithiated samples. However, these authors **identify** Fe_3O_4 and Fe as a coproduct of the reaction. According to our data, neither Fe(II) disproportion or reduction are observed in the thermal treatment in vacuum.

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