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Synthesis and electrochemical behavior of Fe-doped overstoichiometric LiMn_2O_4 -based spinels

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Abstract Ternary oxides of Li-Fe-Mn-O system with overstoichiometric spinel structure $\text{Li}_{1+x}\text{Mn}_{1-y}\text{Fe}_y\text{O}_4$, have been synthesized. The effect of composition and synthesis temperature on the electrochemical performance of the oxides as a material of positive electrodes of Li-ion batteries has been studied. The optimal temperature of synthesis was found to be 850 °C for the composition $\text{Li}_{1.2}\text{Mn}_{1.6}\text{Fe}_{0.4}\text{O}_4$. This oxide shows good reversibility at acceptable level of capacity near 105 mAh/g.

Introduction

Lithium manganese spinel, LiMn_2O_4 , is considered to be one of the most attractive cathode materials for Li-ion batteries as an alternative to LiCoO_2 for cost and toxicity reasons [1]. Emphasis was placed both on understanding of its structural aspects and on the elaboration of LiMn_2O_4 materials through various chemical means. However, the electrochemical properties of LiMn_2O_4 are highly dependent on the synthesis route, processing conditions, and thermal history of the samples [2].

The structure of the spinel LiMn_2O_4 consists of a cubic close-packed oxygen array in which the lithium ions are located at the 8a tetragonal sites and the manganese ions at the 16d octahedral sites of a cubic unit cell with space group $Fd\bar{3}m$. The galvanostatic behavior of $\text{Li}_x\text{Mn}_2\text{O}_4$ electrodes is characterized by two voltage plateaus at around 3 and 4 V (vs. Li/Li^+). The 4 V plateau includes two closely spaced subplateaus, around 3.95 and 4.1 V. The 4 V plateau is used for practical batteries applications (with x in

$\text{Li}_x\text{Mn}_2\text{O}_4$ ranging from 0 to 1, which correspond to a theoretical specific electrode capacity of 148 mAh/g). The lithium ions remain on tetragonal sites within cubic structure for the range $0 < x < 1$.

Much less information is available on the behavior of this material around 3 V (vs. Li/Li^+). The electrode process results in a cubic-to-tetragonal phase transition as x in $\text{Li}_x\text{Mn}_2\text{O}_4$ increases from 1 to 2. However, the practically attainable specific capacity is considerably less than the theoretical value of 148 mAh/g. [3]. The Jahn-Teller distortion is observed in samples with compositions close to LiMn_2O_4 with an average oxidation state below +3.5 for Mn [4]. The insertion of lithium into LiMn_2O_4 occurs at 3 V for $1 < x < 2$; it causes a first-order transition to rock salt phase $\text{Li}_2\text{Mn}_2\text{O}_4$ during which the tetrahedrally coordinated lithium ions are cooperatively displaced into octahedral sites (16c). The large anisotropic (Jahn-Teller) distortion ($c/a = 1.16$) is generally believed to be largely responsible for poor cycling behavior of the spinel electrode at 3 V.

The stabilization of $\text{Li}_x\text{Mn}_2\text{O}_4$ spinel structure could be achieved by means of partial heterovalent substitution of manganese with other transition cations. This would increase the average oxidation number of Mn at the end of discharge, and thus, suppress the Jahn-Teller distortion and improve the cycleability of the material. The substitutes with Ni, Co, Cu have been reported in [5, 6, 7, 8, 9, 10].

In the present work, we have studied the process of heterovalent substitution of manganese cations for Fe^{3+} cations in the spinel array.

Experimental

Samples of $\text{Li}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_4$ powders were prepared by a molten precursor method for rapid sample homogenization at relatively low temperature. For each product, the required amounts of powdered chemicals were mixed and preheated in the range of 150–300 °C. After the reaction, products were ground in agate mortar and finally calcinated at 400, 700 and 1000 °C, respectively (Table 1). After milling, the powders of complex oxides were characterized by XRD, SEM and chemical analysis.

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Table 1 Synthetic conditions of spinel phases preparation in Li-Mn-Fe-O system

Sample	Li/Mn/Fe-precursors ratio	Duration of final heating (h)	Temperature of final heating (°C)
A	1.2/1.6/0.4	4	400
B	1.33/1.33/0.67	4	400
C	1.2/1.6/0.4	1.5	700
D	1.33/1.33/0.67	1.5	700
E	1.2/1.6/0.4	1.5	850
F	1.33/1.33/0.67	1.5	850
G	1.2/1.6/0.4	1.5	1000
H	1.33/1.33/0.67	1.5	1000

Electrochemical activity of the products (Li intercalation) was studied in experimental coin cells of 2016 size. The electrode active masses were prepared by mixing the active material with 10 wt.% of Lonza graphite and 5 wt.% of polyvinylidene fluoride slurred in 1-methyl-pyrrolidone solvent.

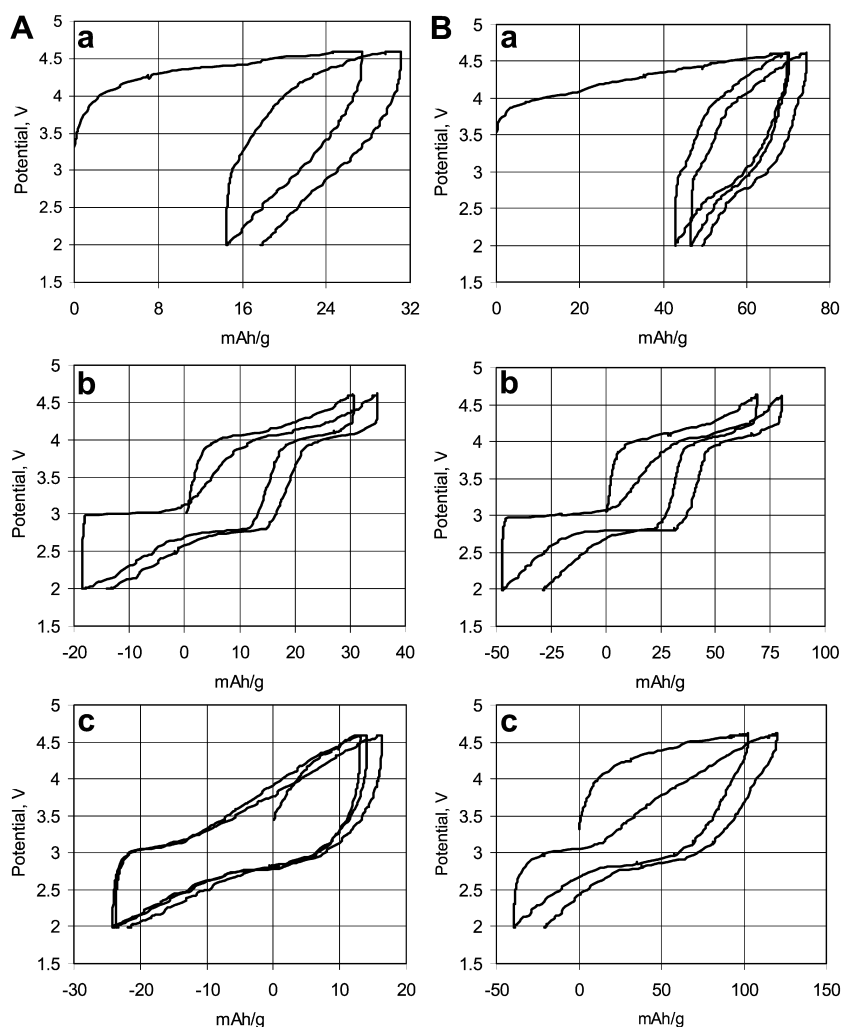
The mass was then pasted onto one side of pre-cleaned Al foil, dried for 4 h at 100 °C, pressed and the disks of 15.6 mm diameter were cut and placed into the cell's coins. Large excess of Li metal (foil) was used as an opposite electrode. A solution of 1 M LiPF₆ in mixture of ethylene carbonate (50 vol.%) and methyl carbonate was used as an electrolyte (Merck product LP30). The assembled cells were then tested by linear sweep voltammetry (LSV) (potentiostat PI50) and/or galvanostatic charge-discharge (PC governed automatic bench) methods.

Results and discussion

In the present work, the chemical compositions of prepared samples series Li_xMn_{1-y}Fe_yO₄ were chosen to attain the +3.5 oxidative state of manganese cation. For all samples the overstoichiometric quantities of lithium compounds were used ($x > 1$) for compensation of dopant cation low charge.

The XRD patterns of the powders, which were obtained at 400 °C, show broad weak peaks. All peaks are attributed to spinel phase. At such low temperature

Fig. 1 **A** The profile of first cycles curves for samples H (a), D (b) and B (c). Rate≈0.25C. **B** The profile of first cycles curves for samples G (a), C (b) and A (c). Rate≈0.25C



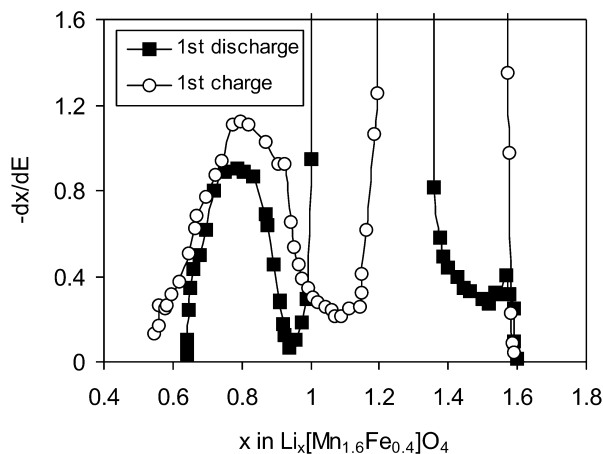


Fig. 2 The differential capacity for $\text{Li}_{1.2}\text{Mn}_{1.6}\text{Fe}_{0.4}\text{O}_4$ prepared at $700\text{ }^\circ\text{C}$ (C)

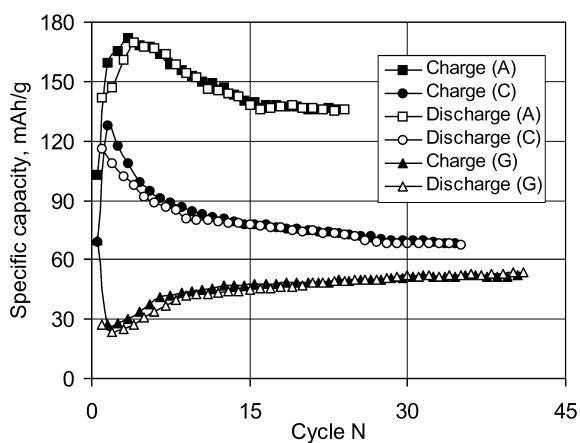


Fig. 3 Specific capacities vs. cycle number in 2–4.5 V limit for A, C, G samples

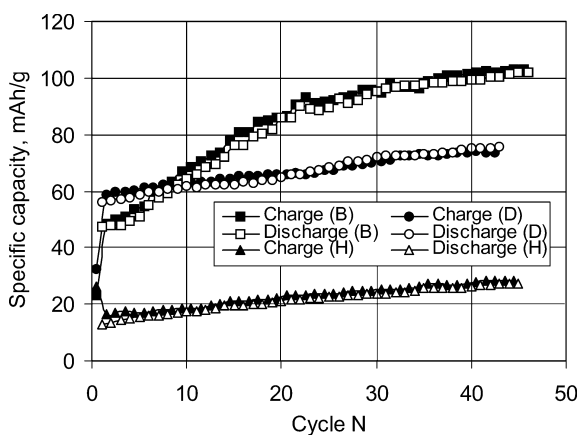


Fig. 4 Specific capacities vs. cycle number in 2–4.5 V limit for B, D, H samples

as $400\text{ }^\circ\text{C}$ the onset of spinel phase formation on the field of amorphous matrix has been identified. The increase of synthesis temperature to $700\text{ }^\circ\text{C}$ results in

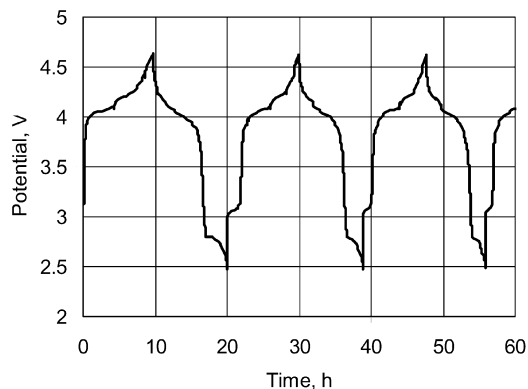


Fig. 5 Galvanostatic charge and discharge curves for sample E in 2.5–4.5 V limit

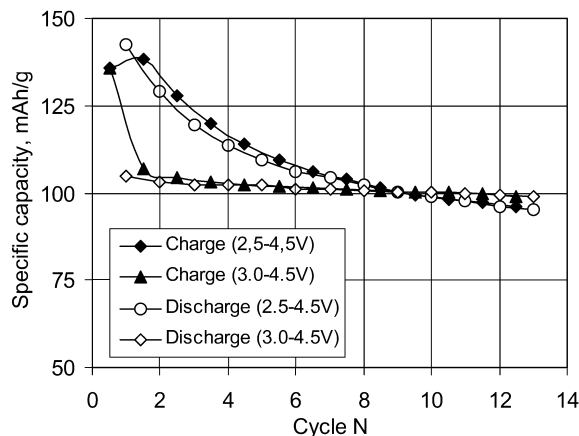


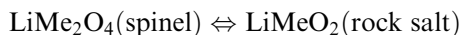
Fig. 6 Specific capacities vs. cycle number for sample E in 2.5–4.5 V and 3.0–4.5 V limits

rapid formation of spinel phase with slight tetragonal distortion. According to XRD data, at the synthesis temperature $1000\text{ }^\circ\text{C}$ $\text{Li}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_4$ spinel is unstable. Some additional peaks were identified in the X-ray diffractogram.

The synthesis temperature has an essential effect on electrochemical behavior of lithium deintercalation/intercalation into the obtained materials. One can see it in Fig. 1, where the voltage profiles of the first charge-discharge cycles are shown for the samples A, B, C, D, G, H.

As follows from the data obtained, the $1000\text{ }^\circ\text{C}$ phases are electrochemically active at the potentials higher than 4.5 V vs. Li, that is, above the limits of electrochemical window of the electrolyte. That is why the attained capacities were rather low. These are increasing in course of cycling and stabilizing near 30 and 60 mAh/g.

The samples prepared at the $700\text{ }^\circ\text{C}$ exhibit two reversible plateaus at 4 and 3 V. As can be seen (Fig. 1), the galvanostatic curve for 3 V process have I-type form. This can be a result of a two phase reaction mechanism due to the formation of rock salt structure:



The divergence of differential capacity plot vs x at $x \approx 1.2-1.4$ (Fig. 2) maintains this conclusion. The total reversible capacity of both 4 and 3 V processes at first cycle are near 130 mAh/g (Figs. 3, 4).

Decrease of synthesis temperature (400 °C samples) leads to diminishing of 4 V plateau. The main part of observed capacity is related to 3 V process. The galvanostatic curves have a J-type form, which is attributed to solid solution formation mechanism:



These samples show good cycle retention and acceptable specific capacity near 155 mAh/g (Figs. 3, 4).

The partial substitution of Mn on Fe in the spinel framework improves the material cycleability when tested in narrow potential range near 4 or 3 V. However, fast structure degradation is observed when cycling in wider voltage range (2–4.6 V).

The temperature of 850 °C is close the optimum value for preparation 4 V material (Figs. 5, 6). In this case the 3 V electrochemical activity is small. The electrochemical performance and chemical analysis data may be attributed to composition $\text{Li}_{1.1}[\text{Mn}_{1.55}\text{Fe}_{0.39}\text{Li}_{0.06}]\text{O}_4$, where the part of lithium cations have occupied the additional tetrahedral sites.

According to obtained experimental data, the total effect of temperature condition on product composition and electrochemical behavior is related to oxygen losses and 3d metal reduction when the temperature increases. This is result of Li cation distribution between octahedral and tetrahedral sites.

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