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Nanostructured Iron-Substituted Lithium-Manganese Spinel as an Electrode Material for Hybrid Electrochemical Capacitor

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Structure, morphology and electrochemical properties of iron substituted lithium manganese spinel were investigated. The cyclic capability of obtained materials in aqueous electrolyte was studied. The kinetic characteristics of Li^+ -ions charge–discharge intercalation were determined.

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1. Introduction

Hybrid capacitors (HC) are one of the most promising modern electric energy power sources and can successfully replace lithium battery in many branches (electric transport, portable electronics) [1]. The performance of HC depends on the peculiarities of surface adsorption and redox reactions. Polarized electrode is typically based on different carbon materials [2]. Lithium-manganese spinel is one the best materials for redox electrode due to high ion and electron conductivity [3]. The disadvantage of these materials is a structure distortion during charge/discharge process. This is the main reason for investigations of spinel crystal structure substitution for lattice stabilization in particularly by iron cations [4]. Simultaneously this is a way for electrode material both conductivity increasing and lithium ions diffusion coefficient enlarging. The aim of the paper is investigation of ultrafine $\text{LiMn}_{1.95}\text{Fe}_{0.05}\text{O}_4$ spinel as Faraday's electrode of HC.

2. Experimental details

$\text{Mn}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as precursors. An aqueous solution of salts in stoichiometry molar ratio have been mixed with gel formation and aging. Obtained gel was annealed at 1073 K. Structure and morphology of the material were investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), the Mössbauer spectroscopy and low temperature nitrogen absorption. Nanoporous carbon was obtained by raw plant materials carbonisation and activations at 673 K during 4 h. The electrochemical properties of material were studied with three-electrode

cells in aqueous 1 M Li_2SO_4 solution. The working electrode was a mixture 75 mass% of spinel and 25 mass% of carbon black.

3. Results and discussion

Thermogravimetric and differential thermal analysis showed a single phase formation in the temperature range 600–800 K with the finishing of solid state reaction at about 900 K (Fig. 1). The obtained materials (predicted formulae $\text{LiMn}_{1.95}\text{Fe}_{0.05}\text{O}_4$) have spinel structure (space group $Fd\bar{3}m$) with lattice constant of 0.8261 ± 0.0325 nm (Fig. 2). The lithium ions occupy the tetrahedral sites of spinel structure while iron and manganese are in octahedral positions. The Mössbauer spectra consist of magnetic sextet (61%) corresponding to high-spin Fe^{3+} in octahedral sites and two doublets. Data analysis was performed accordingly to [5]. Major (37%) and minor (about 2%) doublets correspond to Fe^{3+} and Fe^{2+} ions

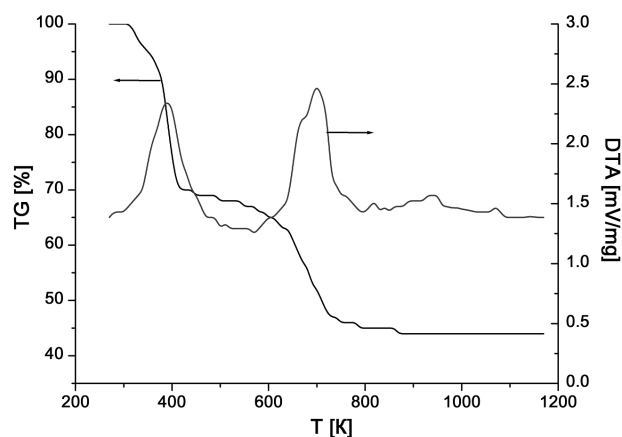


Fig. 1. TG and DTA curves of initial oxides mixture containing gel.

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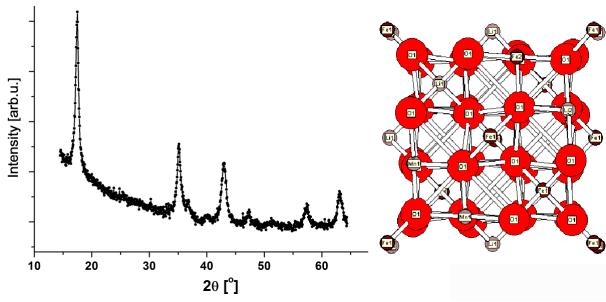


Fig. 2. X-ray diffraction patterns and visualization of $\text{LiMn}_{1.95}\text{Fe}_{0.05}\text{O}_4$ lattice.

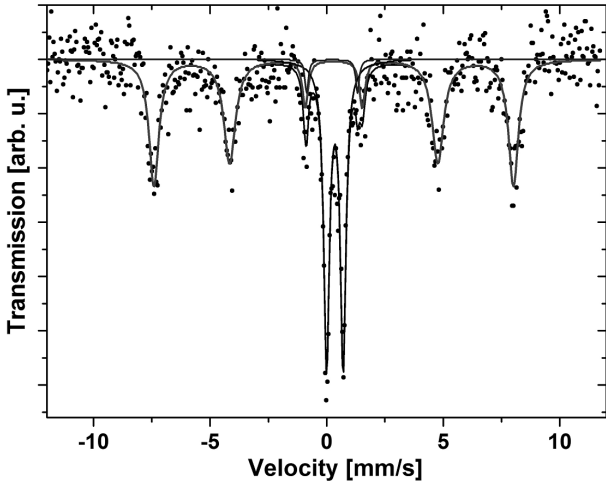


Fig. 3. The Mössbauer spectra of $\text{LiMn}_{1.95}\text{Fe}_{0.05}\text{O}_4$ sample.

in octahedral oxygen coordination (accordingly to calibration of quadrupole splitting and isomer shift), respectively (Fig. 3). The presence of Fe^{2+} impurities is probably caused by the surface reduction during the particle sintering [6]. Average sizes of X-ray coherent scattering areas (the Scherrer equation) are about 12–15 nm. The ultrafine particles form polycrystal agglomerates with the size about 80–100 nm during high temperature annealing (Fig. 4). The specific surface area (BET) was about

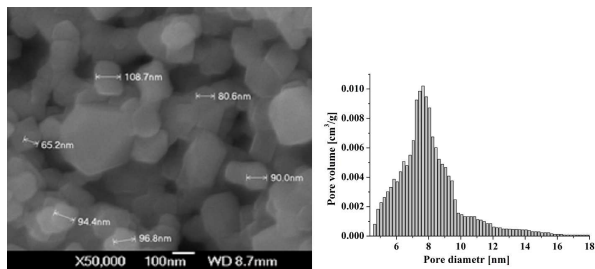


Fig. 4. SEM image of $\text{LiMn}_{1.95}\text{Fe}_{0.05}\text{O}_4$ spinel particles and pore size distribution.

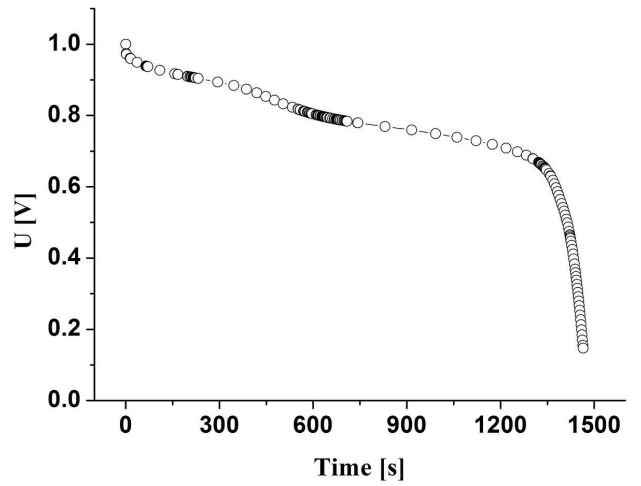


Fig. 5. Galvanostatic discharge curves of three-electrode cell with an electrode on the base of $\text{LiMn}_{1.95}\text{Fe}_{0.05}\text{O}_4$ spinel.

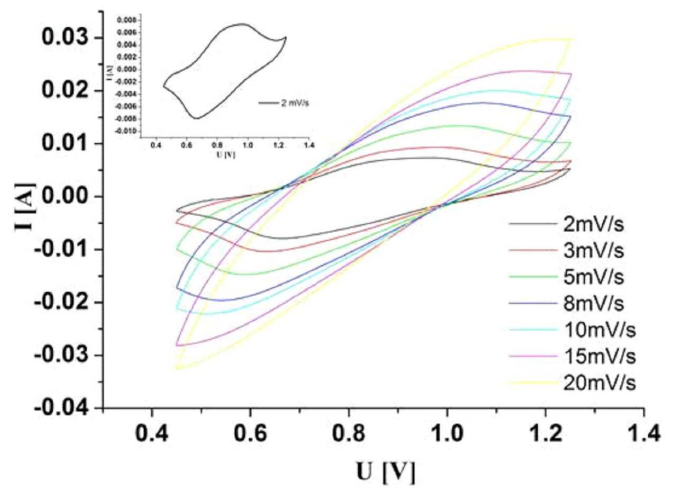


Fig. 6. CVA-curves obtained at different scanning rates (2–20 mV/s).

$32 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution has a maximum at about 8 nm. The average pore sizes are close to the size of primary particle.

The discharge curves of electrode based on the obtained material demonstrate a sloping of voltage in ranges about 0.9–0.8 V (comparatively the chlorine-silver electrode) and capacity 13 mAh/g (Fig. 5). Cyclic voltammograms (CVA) were obtained at scan rates (2–20 V/s) (Fig. 6). CVA curves at low scan rates are characterized by redox peaks at 0.60–0.65 V which associated with reversible Li^+ ions intercalation. The reduction peaks shift negatively and the oxidation peaks shift positively with the scan rate increasing. The diffusion coefficient (D) was calculated from the CVA data using linear approximation of i_p vs. $\nu^{1/2}$ plot [7]: $i_p = 2.99 \times 10^5 (\alpha n)^{1/2} A \Delta C D_{Li}^{1/2} \nu^{1/2}$ (where i_p — peak cur-

rent, ν — scan rate, A — the electrode area, α — transfer coefficient, C — Li-ion molar concentration in electrode, n — number of electrons transferred in the redox process ($n = 1$), F — Faraday constant, R — gas constant, T — temperature. The obtained value of diffusion coefficient is in a range $(2.5\text{--}6.5)\times 10^{-12}$ cm² s⁻¹. This result indicates the 3D-arrangement of intercalated ions during the intercalation.

4. Conclusions

The iron substituted lithium manganese spinel LiMn_{1.95}Fe_{0.05}O₄ synthesized by sol-gel method is the promising electrode materials for hybrid capacitors. The presence of Fe²⁺/Fe³⁺ redox couples and increased accessible surface area to electrolytes are the additional factors to enhanced pseudocapacitive contribution for charge storage mechanism. Li⁺ ions diffusion coefficient slightly depends on the scan rate and changes in the range of $(2.5\text{--}6.5)\times 10^{-12}$ cm² s⁻¹.

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