Original Research

The ultrasonic modification of thermodynamic and kinetic regularity of lithium intercalation in talc ☆

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Abstract

Influence of the ultrasound on talc ($Mg_3Si_4O_{10}(OH)_2$) cathode material was experimentally investigated. The Gibbs' energy change of the Li^+-intercalation process, the diffusion coefficient in $Li_xMg_3Si_4O_{10}(OH)_2$, the charge transfer resistance and the capacitance of the electric double layer were studied in electrochemical cells, based on initial and ultrasonic treated talc. The obtained results were interpreted within the nonlinear diffusion-deformation model, which involved formation of vacancy nanoclusters under ultrasonic influence at temperatures lower than a critical value.
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1. Introduction

Intercalation is the reversible insertion of molecule (or ion) into guest position of compounds with layered structures. Furthermore, intercalation provides a significant increase in specific energy of power sources, because strongly correlated bertollide phases are formed as a result of current generation process. The technical implementation of such process causes the appearance of lithium and lithium-ion batteries at the market. Today searching of new cathode materials for these applications is almost the most important task of material science. Taking into account the urgent problems of high prices of one Wh, ecological compatibility and resource base formation for use in the foreseeable future, it is obvious to focus on natural minerals. For this purpose they should have a system of the guest positions and provide good lithium diffusion and energy of lithium insertion, chemical and electrochemical stability, appropriate structure of the energy spectrum

[1] conjugated with voltage range. We have proved that talc could be this mineral [2]. However, generally, the combination of all above listed characteristics in a certain mineral is implemented rarely. Therefore target modification of talc takes a lead place in improving efficiency of intercalation reaction. It was shown [3] that doping of talc powders could change its band structure in desired direction and as a result could improve both the energy and the power characteristics of lithium power sources. In this paper, we proposed ultrasonic treatment [4–6], as a new method of modification, which belongs to one of the most effective, cheap and environmentally safe technologies.

2. Experimental

Monodispersed talc powders with average grain size of 1 and 0.5 μm were used in experiments. Ultrasonic treatment of each talc fractions (0.2 g) was carried out in 2 ml of 1 M $LiBF_4$ in γ-butyrolactone solution during 8 h at the frequency of 22 kHz.

Electrodes of 0.25 cm^2 area on a nickel substrate were formed for research. The cathode mixture consisted of active

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material (talc), conductive additive (acetylene soot), binding agent in the ratio 85:10:5 wt%. Mass of active material did not exceed 2.5 mg/electrode. Thermodynamic and kinetic parameters of lithium intercalation were investigated in three-electrode electrochemical cell in 1 M $LiBF_4$ in γ-butyrolactone solution and a chlorine-silver reference electrode. Nyquist diagrams were investigated in the frequency range from 10^{-3} to 10^6 Hz using impedance spectrometer "AUTOLAB" ("ECO CHEMIE", Netherlands), equipped with computer applications FRA-2 and GPES. Computer modeling of the obtained impedance data was carried out in the software package ZView 2.3 (Scribner Associates). X-ray diffraction (XRD) measurements were performed on a DRON-3 under Co-Kα-radiation.

3. Results and discussion

Dependence of Gibbs' energy change ($\Delta G(x)$) of Li^+-intercalation process in talc fractions before and after ultrasonic treatment vs. the guest load degree x (x is a number of inserted guest atoms per one structural unit of host material) is shown in Fig. 1. First of all, one should pay attention to the behavior of curves 1 and 2 in Fig. 1. Since reduction of initial talc powders size from 1 μm to 0.5 μm leads to disappearance of the Ist order phase transition in x range from 0 to 2.5 and formation of strongly correlated single-phase states. The 1 μm talc fraction has higher energy storage in the high lithiated phases ($x > 4.5$). After ultrasonic treatment of talc fractions the phase diagram of their intercalated phase has changed completely. The range of two-phase states of the 1 μm fraction is divided into three intervals: with higher ($0 < x < 0.8$), lower ($0.8 < x < 1.5$) and ($1.5 < x < 4.5$) energy storage. The range of two-phase states of the 0.5 μm fraction changes both width ($0.8 < x < 3$) and values of ΔG ($3 < x < 5$).

Kinetics of Li^+-intercalation processes in Li_xMg_3-$Si_4O_{10}(OH)_2$ at room temperature both before and after ultrasonic treatment (Fig. 2) cannot be described by the Rendls–Ershler classical model [7] because the slope angle of the low frequency branches of Nyquist plots to Re Z axis of the complex impedance differs from 45°. The most probable
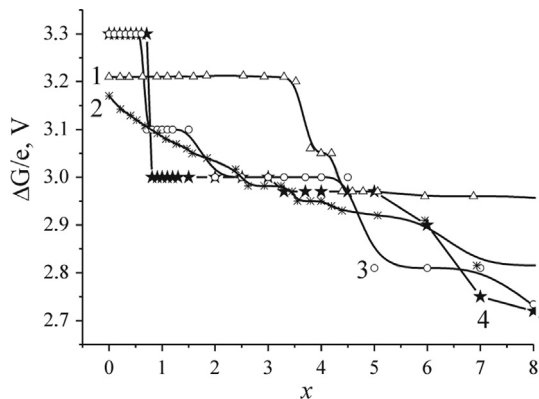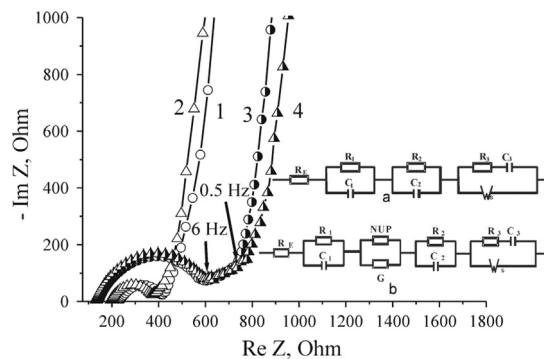

Fig. 2. Nyquist diagrams of 1 μm (1, 3) and 0.5 μm talc fractions (2, 4), before (1, 2) and after (3, 4) ultrasonic modification. The insets are equivalent electric circuits.

reason for this is that the lithium diffusion in the volume of talc particles is not described by the ideal Fick's law. This in turn provides application of finite Warburg impedance [7] as a structural diffusion element in the impedance model. In the proposed equivalent electrical scheme (inset a, Fig. 2) R_E is resistance of an electrolyte, the series of parallel units of $R_1\|C_1$ and $R_2\|C_2$ consecutively attached to the Rendls–Ershler modified chain $W_s\|(R_3-C_3)$ simulates charge transfer through the barriers between grains (and possibly passivation film) and through the space charge region in the talc particle, respectively.

Computer modeling of the obtained impedance data in the software package ZView 2.3 determines the kinetic parameters of the intercalation process for all values of x. Verification of adequacy of the constructed model to the experimental data shows that Kramers–Kroning's coefficient does not exceed 3×10^{-5}.

Nyquist plots indicate the diffusion-kinetic control of the intercalation process. It means that limiting parameters of power capability are the lithium diffusion $D(x)$ in talc and the charge transfer resistance $R_3(x)$ through the interface of talc and electrolyte. As it is shown in Fig. 3 the kinetic parameters essentially depend on the conditions of ultrasonic effect on talc. At the same time ultrasonic treatment significantly increases power capacity even at sufficiently deep discharge levels ($x \approx 4$). It is interesting to note that the Ist order phase transitions (Fig. 1) are observed in the vicinity of this value of x. Extraordinary is the fact that both $D(x)$ and $R_3(x)$ oscillate with concentration only after ultrasonic modification (insets, Fig. 3). Hypothetically, such behavior can be explained by changes in electronic energy topology caused by ultrasonic effect on defective subsystem.

The XRD analysis of both samples before and after intercalation confirms impact of ultrasound on defect subsystem. First of all, aftereffect of ultrasonic treatment on the talc structure depends on the particle size. Ultrasonic treatment of the 1 μm fraction greatly reduces the width of the main peaks at $2\Theta = 11.00$ and 33.39°. Moreover treatment reformats the intense doublet at $2\Theta = 22.05$ and 22.59° into one peak at $2\Theta = 22.17°$. Ultrasonic treatment of the 0.5 μm fraction reduces intensity of the indicated diffraction peaks and slightly

Fig. 1. Gibbs' energy change of lithium intercalation process in talc $Mg_3Si_4O_{10}(OH)$ powder of fractions: 1 μm (1, 3) and 0.5 μm (2, 4), before (1, 2) and after (3, 4) ultrasonic treatment.