JPNU
scientific journal

THERMODYNAMIC PARAMETERS OF THE INTERCALATION REACTION IN THERMAL AND LASER MODIFIED NANODISPERSED ANATASE

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Abstract. It is modified matrix of anatase in turn of the thermal and laser treatments. The dependence of Gibbs energy change of the intercalation reaction of lithium with the guest load degree change was analyzed. Laser irradiation turned out to increase twice the value of maximum lithium "guest" loading, constricting heterophase area and changing contrarily concentration genesis of temperature dependence of entropy of lithium dilution. The optimal conditions of laser irradiation nanodispersive anatase (pulse energy E = 0,02 J, pulse duration τ = 15 ns repetition frequency f = 28 Hz, duration of exposure to 5 min.), at which specific energy characteristics of LPS, formed on its basis, increased by 55% is set.

Keywords: degree of intercalation, anatase, laser irradiation, specific capacitance.

1. INTRODUCTION

Transition metal oxides are promising electrode materials in advanced high-energy density batteries. The performance of an electrode depends on its ability to intercalate lithium reversibly into the host lattice. The transition metal oxides have open structures capable of accommodating guest ions and a flexible electronic structure which can accommodate donated electrons and provide sufficient ionic and electronic conductivity. One material which promises excellent properties for technological use as an electrode material in lithium batteries is anatase.

Nowadays, the problem of increasing power generation per unit mass and unit volume of a power source active substance is of paramount importance. The transition to nanosize of particles of cathode active material, which participate in Li+–intercalation current generating reaction, is one of the most effective methods to solve this problem [1, 2]. However, the problem of the possibility of ensuring essential increase of specific capacity in cathode process remains unsolved yet. Therefore, the aim of this work is an attempt to solve this problem.

2. EXPERIMENTAL SETUP

The solution of the set problem with taking into account the necessity of ensuring a high concentration of guest positions should be searched in the choice of such technique of modifications

which could enable us to control defects caused by growth (they can become additional guest positions as well) and impurity subsystem, with the necessary topology of energy levels in the gap.

Anatase was modified in vacuum 10^{-6} Pa at temperature 500 and 700°C during 1 h. Laser modification of nanodispersed anatase caused by action of laser irradiation (τ_i = 15 ns λ = 1.06 μm) with pulse energy 0.02, 0.03 and 0.04 J (duration of exposure to 5 min). For electrochemical investigations, electrodes with the area of 0.5 cm^2 on Ni substrate were formed. The electrode consisted of titanium dioxide powder, acetylene black as a conductive admixture and the binding agent, in the mass proportion of 85%: 10% : 5%. The mass of nanodispersed titanium dioxide did not exceed 3 mg. Thermodynamic electrochemical laws of lithium intercalation have been investigated in a three-electrode cell with one-mole solution of LiBF$_4$ in $\gamma°$-butyrolactone, a lithium electrode, and a lithium reference electrode.

3. EXPERIMENTAL RESULTS

The "guest" load degree and specific capacity is given in Table 1. In order to ascertain the degree of correlation between energy topology of impurity subsystem and the process of Li$^+$–intercalation current generation, thermodynamical investigations according to EMF technique [3] were carried out. The results of the analysis of the behavior of Gibbs' energy change $\Delta G(x)$ as function of the guest load degree for both materials are given in Fig. 1. It can be seen that the magnitude of the degree of guest load increases for modified anatase under discharge down to the voltage of 1.5 V, as compared to original anatase.

Temperature of thermal modification t,°C.	Pulse energy E, J	"Guest" load degree of Li$^+$	Specific capacity, A·h/kg
Original anatase	0	1,8	620
	0,02	2,7	887
	0,03	2,3	776
	0,04	1,5	492
500	0	2,9	971
	0,02	3,3	1115
	0,03	3,5	1182
	0,04	2,7	901
700	0	2,4	802
	0,02	4,4	1378
	0,03	3	998
	0,04	2,1	705

Tab. 1. The "guest" load degree and specific capacity of modified anatase.

The following equation can help to understand the process [4, 5]:

$$\Delta G(x) = eE(x) = \mu_i(x) - \mu_0, \tag{1}$$

where $\Delta G(x)$ is the change of the Gibbs energy of the reaction, e is the charge of electron, E is the electromotive force of the reaction, $\mu_i(x)$ is the chemical potential of the lithium insertion into the host structure, μ_0 is the chemical potential of lithium in the metallic lithium anode, x is the number of lithium atoms per unit of the host material according to the formula.
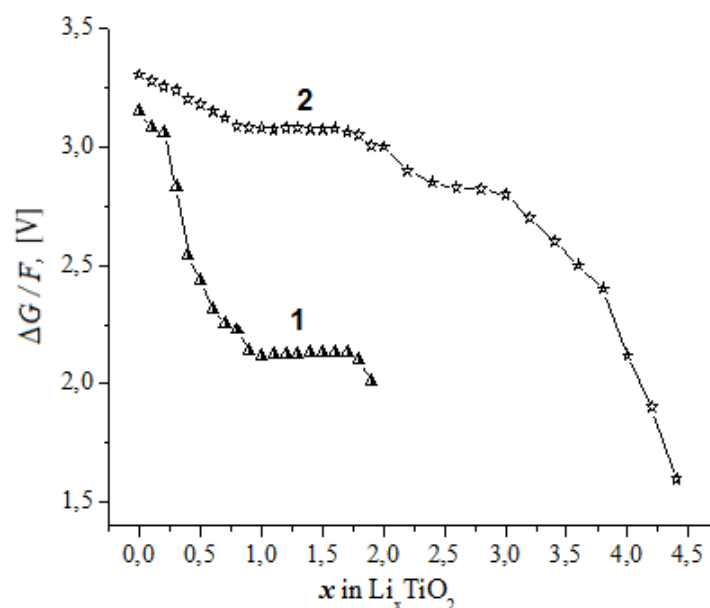
Fig. 1. Dependence of the Gibbs energy on guest load degree in original anatase (1) and modified anatase (2).

From the point of view of the thermodynamics of the Li+-intercalation current generation and according to Eq. (1), such transition means a change in the behaviour of $\mu_i(x)$. Its dependence on the degree of guest load x can be represented by the equation [6]:

$$\mu_i(x) = kT \ln \left| \frac{x}{1-x} \right| + N\omega x + [E_F(x) - E_F(0)] + L \frac{\partial c}{\partial x} + E_0. \qquad (2)$$

Here k is the Boltzmann constant, N is the number of the nearest neighbouring places, ω is the energy of interaction of inserted guest components, E_F is the position of the Fermi level, C is the distance between the layers, L is the coefficient which is determined by the Lennard–Jones potential function, E_0 is the bonding energy between intercalated atoms and matrix layers. It is evident that the change in $\mu_i(x)$ causes a change in the structure of the discharge curve.

4. CONCLUSIONS

Carried out investigations unambiguously indicate that the thermal and laser modification of structure of particles generating energy in Li+-intercalation leads to pronounced increase in specific energy and power. However, just this modification does not ensure essential approaching of practically implemented specific capacity to the theoretically possible maximal value of corresponding cathode process. It ensures a magnitude at a level which does not exceed 1/3 of the theoretically possible one, relatively to the electrochemical equivalent of lithium. We have proved that the solution of the problem of further increase in specific capacity for nanodispersed anatase can be attained through forming structure defects; these defects form a certain energetic topology of electron states. And through this topology the defects formation ensures the needed dependence in the form of a function of lithium chemical potential of guest load degree.

According to the aforesaid approach, the physical mechanism of essential increase in energy and specific capacity consists in such a change of the energetic topology of a defects subsystem when:

- the density of states at Fermi level increases;
- deep levels in gap emerge.

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Сегін М.Я., Будзуляк І.М., Морушко О.В., Яблонь *Л.С.* Термодинамічні параметри інтеркаляції в термічно та *лазерно модифікований нанодисперсний анатаз. Журнал Прикарпатського університету імені Василя Стефаника*, **3** (1) (2016), 71–74.

Проаналізовано залежність зміни енергії Гібса реакції від ступеня інтеркаляції іонів літію в модифікований термічним та лазерним відпалом анатаз. Лазерне опромінення викликає двократний ріст максимального гостьового навантаження іонів літію та зміни температурної залежності ентропії розчинення літію в матриці анатазу. Встановлено оптимальні умови лазерного опромінення (енергія імпульсу E = 0,02 Дж, тривалість імпульсу τ = 15 нс, частота f = 28 Гц, витримка 5 хв), при яких питома ємність літієвого джерела струму зростає на 55 %.

Ключові слова: ступінь інтеркаляції, анатаз, лазерне опромінення, питома ємність.