


## Li-ion Diffusion in Porous Carbon Electrode Materials by GITT Method

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The process of diffusion of lithium ions into porous carbon electrode materials obtained by hydrothermal carbonization of plant raw materials at different temperatures was the galvanostatic intermittent titration technique. The diffusion coefficient of lithium ions in the electrode material was calculated and its dependence on the intercalation degree  $x$  was analyzed. It was found that with the increase in the carbonation temperature of the raw material, which results in the removal of gaseous aliphatic and then aromatic molecules with low molecular weight, processes of cyclization and aromatization of molecules, as well as intensive carbonization of the raw material, the formation of carbon layers and primary graphite nuclei, the coefficient diffusion increases due to ordering the structure of the porous carbon material and reducing its specific surface area and total pore volume. When the maximum value of the intercalation degree is reached, the diffusion coefficient of lithium ions is  $3.6 \cdot 10^{-12} \text{ cm}^2/\text{s}$  ( $x = 0.28$ ),  $7.9 \cdot 10^{-12} \text{ cm}^2/\text{s}$  ( $x = 0.44$ ), and  $1.9 \cdot 10^{-10} \text{ cm}^2/\text{s}$  ( $x = 0.19$ ) for samples obtained at carbonization temperatures of 600, 750, and 1000 °C, respectively. A comparative analysis of the values of the diffusion coefficient, calculated on the basis of the data of galvanostatic intermittent titration technique and electrochemical impedance spectroscopy, was carried out.

**Keywords:** Porous carbon material, Lithium ion, Intercalation degree, Diffusion coefficient, Galvanostatic intermittent titration technique.

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### 1. INTRODUCTION

Nowadays, porous carbon materials (PCMs) are widely used as an active component of electrode materials of lithium power sources [1-4] and electrochemical capacitors [5-7]. The main requirement for their use in lithium power sources, and especially lithium-ion batteries, is the ability to provide high specific power. The power density can be significantly affected by the rate of diffusion of lithium ions in active electrode materials, which is determined by the diffusion coefficient  $D$ . A number of experimental methods are used to determine the diffusion coefficient, which include the current pulse relaxation method [8], potentiostatic intermittent titration technique [9], galvanostatic intermittent titration technique [10, 11], intermittent current interruption [12], electrochemical impedance spectroscopy [11, 13]. The diffusion coefficient of lithium ions into the electrode material largely depends on the type of carbon material used, its crystal structure, morphology, degree of ordering, and its value is in the range from  $10^{-5} \text{ cm}^2/\text{s}$  for highly ordered materials with a structure of graphite to  $10^{-13} \text{ cm}^2/\text{s}$  for disordered turbostratic carbons [14]. The use of various experimental methods to estimate the value of the diffusion coefficient of lithium ions in the same PCMs sometimes leads to obtaining data that can differ by 1-2 orders of magnitude. This requires the use of additional methods to solve the task or review the conditions of the experiment, which sometimes becomes an overwhelming task.

In previous work [15], investigating the prospects of

using PCMs obtained from plant raw materials as electrodes of lithium power sources, we calculated the diffusion coefficient of lithium ions in the electrode material using the electrochemical impedance spectroscopy method and analyzed its dependence on the intercalation degree  $x$ . In particular, it was found that at the initial stage of intercalation ( $0 < x < 0.078$ ) the diffusion coefficient is reduced by 3 orders of magnitude (from  $10^{-8}$  to  $10^{-11} \text{ cm}^2/\text{s}$ ), and at  $x \geq 0.078$  its value is  $4 \cdot 10^{-12} \text{ cm}^2/\text{s}$  at full lithiation of the carbon electrode. The purpose of this work is to determine the diffusion coefficient  $D$  in PCMs using the galvanostatic intermittent titration technique and to compare the obtained data with the results of a previous study.

### 2. EXPERIMENTAL DETAILS

PCMs obtained by hydrothermal carbonization of plant raw materials at temperatures of 600, 750, and 1000°C were selected for the study. Accordingly, the materials studied were denoted as C-600, C-750, and C-1000. The initial material for carbonization was apricot pits, crushed mechanically, which were placed in an autoclave with distilled water. The autoclave was placed in the oven, where the initial PCM was obtained for 1 hour at a constant temperature. The material obtained after the carbonization process was subjected to mechanical grinding twice.

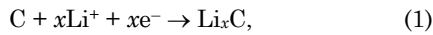
A mixture of active material (PCM) and binding component (teflon) was used for the manufacture of

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lithium power source cathodes in a mass ratio of 96 % : 4 %, respectively. To obtain a homogeneous mixture, these components were mechanically mixed. When acetone was added to the mixture, a paste-like consistency was obtained, which was applied to a  $5 \times 5$  mm nickel grid. The reference electrode was made from lithium foil by pressing it onto a nickel grid. The electrodes were immersed in the electrolyte solution, after which the element was sealed. A one-molar (1M) solution of lithium tetrafluoroborate salt ( $\text{LiBF}_4$ ) in  $\gamma$ -butyrolactone was used as an electrolyte. The production of the electrochemical element was carried out in a dried  $\text{P}_2\text{O}_5$  box filled with argon. The equilibrium electrode potential of PCM relative to the reference lithium electrode was 3.2 – 3.4 V.

When using PCM as a cathode, the main current-generating process can be presented in the form:



where  $x$  is the intercalation degree or the value of "guest" load, which can be determined based on the ratio:

$$x = \frac{M I t}{n F m}, \quad (2)$$

where  $n$  is the number of electrons involved in the reaction,  $M$  and  $m$  are the molar mass and mass of PCM, respectively,  $F$  is the Faraday constant,  $I$  is the discharge current, and  $t$  is the discharge time.

### 3. RESULTS AND DISCUSSION

The galvanostatic intermittent titration technique (GITT) is one of the most accurate methods for determining the diffusion coefficient of lithium ions during processes of electrochemical intercalation / deintercalation in the "host" material [16, 17]. It is based on the chronopotentiometry procedure, during which lithium ions are intercalated (deintercalated) into the electrode material when a small direct current is applied for a limited period of time  $\tau$ , at the end of which the material is characterized by the lithium content  $x \pm \Delta x$  depending on the direction of the current.

The diffusion coefficient of lithium ions into the PCM-based electrode can be calculated using Fick's second law for diffusion with boundary conditions. In the case of small currents and short time intervals, the diffusion coefficient  $D$  is given by the equation [16]:

$$D = \frac{4}{\pi} \left( \frac{m V_M}{M A} \right)^2 \cdot \left( \frac{\Delta E_s}{\tau (dE_\tau / d\sqrt{\tau})} \right)^2 \quad (\tau \ll L^2/D), \quad (3)$$

where  $M$ ,  $m$  are the molar mass and mass of PCM, respectively;  $V_M$  is the molar volume of the formed intercalation compound;  $A$ ,  $L$  are the area and thickness of the electrode, respectively;  $dE_\tau$  is the change in the voltage of the electrochemical element under the applied current over time  $\tau$ ,  $\Delta E_s$  is the value of the voltage relaxation during this time.

In the case of a straight-line dependence  $E = f(\tau^{-1/2})$  (where  $E$  is the voltage of the electrochemical element),

equation (3) is simplified and takes the form

$$D = \frac{4}{\pi \tau} \left( \frac{m V_M}{M A} \right) \cdot \left( \frac{\Delta E_s}{\Delta E_\tau} \right)^2. \quad (4)$$

During the calculations, it was assumed that the molar volume  $V_M$  remains constant with a change in the lithium content in the PVM, and its possible change was neglected.

In order for the dependence  $E = f(\tau^{-1/2})$  to be linear, the discharge current was 10  $\mu\text{A}$ , the discharge time  $\tau$  was chosen equal to 0.3 h, and the relaxation time  $\tau_{\text{rel}}$  of the element voltage to a constant value  $E_s$  was 0.9 h. Under the selected conditions, the element was discharged until reaching the maximum value of the intercalation degree  $x$ . The general form of the chronopotentiogram obtained is similar to the form of the galvanostatic curve. A partial fragment of this dependence with the parameters depicted on it, which are necessary for calculating the diffusion coefficient of lithium ions according to formula (4), is presented in Fig. 1.

Calculations of the diffusion coefficient of lithium ions in PCMs according to formula (4) carried out by the GITT indicate a monotonous decrease in the value of  $D$  with an increase in the intercalation degree  $x$  for all the materials studied (Fig. 2). A sharp drop in the diffusion coefficient at the initial stage of the electrochemical process corresponds to the formation of a near-surface solid layer enriched with intercalated lithium ions, the electrostatic interaction of which complicates the process of further intercalation [15]. A further slight decrease in the diffusion coefficient indicates the stabilization of the process of electrochemical intercalation of lithium ions into the electrode material.

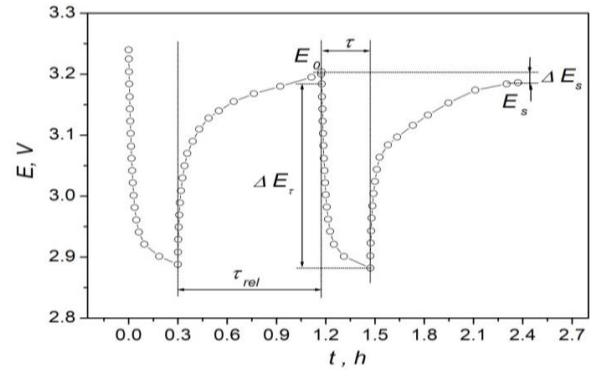


Fig. 1 – A fragment of the GITT curve

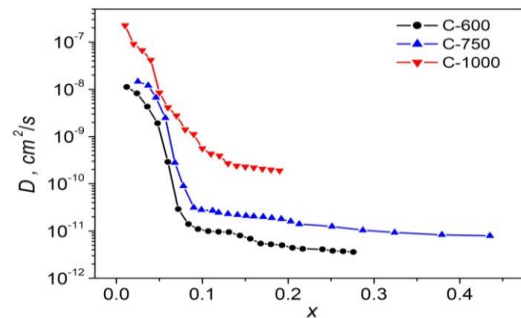


Fig. 2 – The dependence of the diffusion coefficient of lithium ions on the intercalation degree value

For an electrochemical element based on the C-600 sample, the values of the parameter  $D$  are somewhat smaller than for the C-750 sample. Vice versa, diffusion processes involving lithium ions in the C-1000 sample occur faster (Fig. 2). This behavior can be explained primarily by the physico-chemical processes that occur during the carbonization of the raw materials at the given temperatures, and as a consequence by the structural and morphological parameters of the materials obtained. In particular, gaseous aliphatic and then aromatic molecules with low molecular weight are removed at the beginning of the process of carbonization of raw materials, since C-C bonds are weaker than C-H bonds. The processes of cyclization and aromatization of molecules take place along with the removal of hydrocarbons at 600°C [18]. The material obtained at this temperature has a highly disordered structure and a significant specific surface area (357 m<sup>2</sup>/g) and total pore volume (0.186 cm<sup>3</sup>/g) [19]. There is a transition from the stage of cyclization/aromatization of molecules to the stage of their polycondensation and the first carbonization at a temperature of 750°C, as a result of which the structure of the material is slightly ordered and the formation of carbon layers begins [18]. This results in a slight decrease in the specific surface area of the material (343 m<sup>2</sup>/g) and the total pore volume (0.166 cm<sup>3</sup>/g) [19]. This, in turn, leads to an increase in the diffusion coefficient of lithium ions in the C-750 sample compared to C-600 one (Fig. 2). In addition, the intercalation degree of lithium ions into the C-750 material is 1.5 times greater than for C-600. Intensive carbonization of the raw material occurs at 1000°C, which is accompanied by the removal of foreign atoms (primarily in the form of CH<sub>4</sub> compounds), the subsequent formation of carbon layers and the formation of primary graphite nuclei [18]. At the same time, the structure of the material undergoes further ordering, and the specific surface area and pore volume decrease sharply – 45 m<sup>2</sup>/g and 0.031 cm<sup>3</sup>/g, respectively [19]. Due to this, the diffusion coefficient of lithium ions in the C-1000 material is an order of magnitude higher than in the C-750 sample.

When the maximum value of the intercalation degree  $x$  is reached, the diffusion coefficient of lithium ions is  $3.6 \cdot 10^{-12}$  cm<sup>2</sup>/s ( $x = 0.28$ ) for C-600,  $7.9 \cdot 10^{-12}$  cm<sup>2</sup>/s ( $x = 0.44$ ) for C-750,  $1.9 \cdot 10^{-10}$  cm<sup>2</sup>/s ( $x = 0.19$ ) for C-1000.

As mentioned above, the use of different methods for determining the diffusion coefficient of lithium ions in the same material can lead to significant differences in the obtained results. Based on this, it is possible to analyze how the values of the  $D$  parameter obtained by the

GITT method differ from those values obtained by electrochemical impedance spectroscopy [15] for the C-750 sample. As follows from Fig. 3, there is a correspondence in the change of the dependence  $D = f(x)$  obtained by both methods. In addition, there is no increase in the ratio of the value of the diffusion coefficient for the same values of  $x$  by more than an order of magnitude, which is quite a satisfactory result for such different experimental methods. This indicates the legality of using both methods to determine the coefficient of electrostimulated diffusion of lithium ions in PCMs.

Taking into account the fact that the PCMs studied are characterized by a disordered structure in which the lithium ions diffusion is some difficult, it can be stated that the values of the parameter  $D$  of the order of  $10^{-7} \div 10^{-11}$  cm<sup>2</sup>/s obtained in this work are reliable and do not contradict the literature data [14].

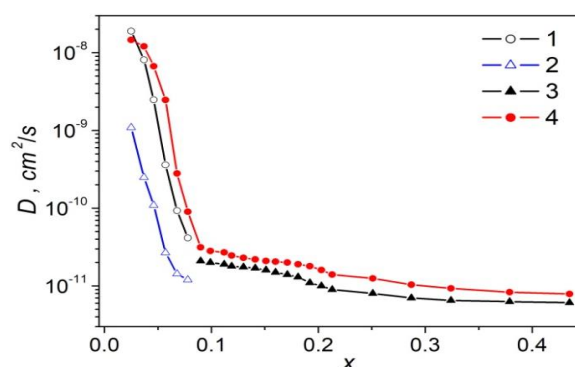


Fig. 3 – The dependence  $D = f(x)$  for PCM C-750 according to electrochemical impedance spectroscopy (curves 1, 2, 3) [15] and GITT (curve 4)

#### 4. CONCLUSIONS

The diffusion coefficient of lithium ions in the porous carbon electrode material obtained by hydrothermal carbonization of plant raw materials at 600, 750, and 1000 °C was calculated using the galvanostatic intermittent titration technique method. It was set that for all materials at the initial stage of lithium ions intercalation ( $x < 0.09$ ) the diffusion coefficient decreases by 3 orders of magnitude. With further intercalation, the value of  $D$  decreases slightly, which indicates the stabilization of diffusion processes in the electrode material. The average deviation of the ratio of the values of the diffusion coefficient, calculated according to the results of galvanostatic intermittent titration technique and electrochemical impedance spectroscopy, does not exceed 2 times.

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## Дифузія іонів літію в пористі вуглецеві електродні матеріали згідно методу гальваностатичного переривчастого титрування

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У роботі з використанням методу гальваностатичного переривчастого титрування досліджено процес дифузії іонів літію в пористі вуглецеві електродні матеріали, отримані гідротермальною карбонізацією рослинної сировини при різних температурах. Розраховано коефіцієнт дифузії іонів літію в електродному матеріалі та проаналізовано його залежність від ступеня інтеркаляції  $x$ . Встановлено, що при зростанні температури карбонізації вихідної сировини, в результаті чого відбувається видалення газоподібних аліфатичних, а потім ароматичних молекул з низькою молекулярною масою, процеси циклізації та ароматизації молекул, а також інтенсивна карбонізація вихідної сировини, формування вуглецевих шарів та утворення первинних зародків графіту, коефіцієнт дифузії збільшується за рахунок впорядкування структури пористого вуглецевого матеріалу та зменшення його питомої поверхні і загального об'єму пор. При досягненні максимального значення ступеня інтеркаляції коефіцієнт дифузії іонів літію становить  $3,6 \cdot 10^{-12} \text{ см}^2/\text{с}$  ( $x = 0,28$ ),  $7,9 \cdot 10^{-12} \text{ см}^2/\text{с}$  ( $x = 0,44$ ) і  $1,9 \cdot 10^{-10} \text{ см}^2/\text{с}$  ( $x = 0,19$ ) для зразків, отриманих за температури карбонізації 600, 750 і 1000°C відповідно. Проведено порівняльний аналіз значень коефіцієнта дифузії, розрахованими на основі даних гальваностатичного переривчастого титрування та електрохімічної імпедансної спектроскопії.

**Ключові слова:** Пористий вуглецевий матеріал, Іон літію, Ступінь інтеркаляції, Коефіцієнт дифузії, Гальваностатичне переривчасте титрування.