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The lithium intercalation into graphite from electrolyte and from solid lithium

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Abstract The values of diffusion coefficient (D) of lithium in thermoexpanded graphite during cathodic intercalation from aprotic electrolyte, and upon direct contact with lithium metal, are measured. In the first case galvanostatic switch-on curves were registered, in the second case the method of x-ray diffraction was used. In the both cases D was close to 10^{-10} cm²/s.

Keywords Lithium diffusion · Lithium intercalation · Thermoexpanded graphite

Introduction

The study of lithium diffusion in carbon materials are of great interest in both theoretical and practical aspects. During recent two decades this process was studied mainly in connection with the development of lithium-ion batteries. Such batteries have negative electrodes based on graphite and other carbon materials. All these researches had dealt with lithium intercalation in the course of cathodic polarization of various kinds of carbon materials in various aprotic electrolytes [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17]. It is significant that the values of the diffusion coefficient (D) reported in these works are in the very wide range, specifically from $10^{-12.5}$ to 10^{-6} cm²/s. This irreproducibility can be explained by variety of experimental conditions as well as by a variety of measuring techniques, including

electrochemical impedance spectroscopy, galvanostatic and potentiometric intermittent titration techniques, cyclic voltamperometry, current pulse relaxation, potential step chronoamperometry and so on. Moreover, the authors reported conflicting data not only about absolute values of D , but about its dependence on the intercalation degree, i.e. on index x in the formula Li_xC_6 . For instance, authors [7, 16] found some increase of D with a rise in x , whereas the contrary result (decrease of D with x rise) was obtained in [3, 5, 6, 12, 13, 14]. D vs x dependence with minimum was described in [8], and such a dependence with maximum was described in [4]. And finally polyextremal D vs x dependence was reported in [9, 10, 11].

Meanwhile, lithium can intercalate into a carbon not only during polarization in an electrolyte but simply with tight contact of the carbon with lithium metal. So, the present work is devoted to comparison of lithium diffusion in graphite during polarization in an electrolyte on the one hand, and during direct contact of dry graphite and lithium on the other hand.

Experimental

All experiments were carried out with thermoexpanded graphite (TEG) [18]. TEG was considered as a promising material for negative electrode of lithium-ion batteries. TEG was prepared by treatment of natural graphite with sulphuric acid with subsequent heat-treatment. TEG powder under study was shown by SEM (JEOL JXA-8600S) to consist of filament-like particles with average diameter ca. 20 μ .

For XRD-study a plate with thickness ca. 0.1 mm was made by pressing of TEG powder. A lithium sheet was brought in tight contact with rear surface of the plate, and this pair was placed in a special cell with beryllium window (Fig. 1). Similar cell for XRD-study was used in [19]; the main difference between both cells consisted in the window material: authors from Israel used the window from polymer film (Mylar). Such cells give a possibility to investigate evolution of XRD-pattern in situ. The cell was assembled in a glove box filled with dry argon. X-ray-diffraction data were collected using a Rigaku D/MAX IIC powder diffractometer (Cu K_α radiation).

Electrochemical measurements were carried out in usual three-electrode cell made from PTFE. In this case working electrodes from TEG were prepared by pressing the powder without a binder

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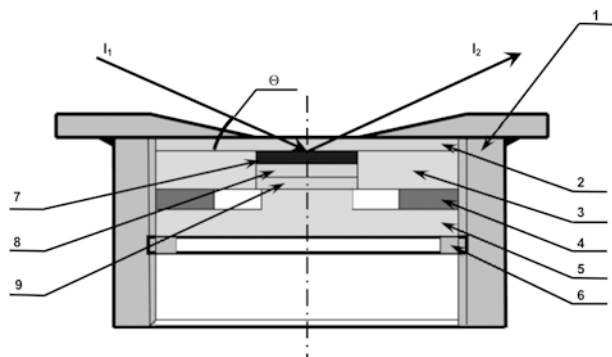


Fig. 1 Cell for XRD measurements. 1 Case, 2 beryllium window, 3 PTFE ring, 4 rubber gasket, 5, 9 PTFE discs, 6 pressing nut, 7 sample (plate of pressing TEG), 8 lithium foil

into a nickel mesh. The electrodes were dried in vacuo at 130 °C for 12 h. Li sheets were used as both counter and reference electrodes. Microporous polypropylene film similar to “Celgard” was used as a separator. 1 M LiPF_6 in a mixture of ethylene carbonate with dimethylcarbonate (LP-30, Merck) was used as an electrolyte. For measurement of dependence of the electrode steady-state potential (E) on intercalation degree x , “quasi-equilibrium” discharge curves with current density 0.5 mA/g were obtained. True E vs x dependences were determined from the cathodic run at third charge-discharge cycle.

To calculate the diffusion coefficient during cathodic intercalation, galvanostatic switch-on curves (E vs t) were recorded with aid of Solartron Electrochemical Interface 1286 and X-Y recorder Endim 622.01. Current density in these experiments ranged from 250 to 1000 mA/g.

Results and discussion

Lithium intercalation during direct contact graphite with lithium metal

XRD-pattern of the initial sample of TEG is shown in Fig. 2. A diffraction peak at $2\theta = 24.88^\circ$ points to the presence of an intercalation compound C_3SO_3 . The compound was formed at sulphuric acid treatment of initial graphite. All other peaks can be ascribed to reflexes from planes (001) for the model of hexagonal 2H-graphite with interlayer distance 0.360 nm.

The contact of the graphite with lithium metal resulted in change of XRD-pattern due to Li intercalation (Fig. 3). In particular C_3SO_3 reflex disappeared and XRD profile became fully corresponding to that of lithiated graphite. No interaction products of Li and SO_3 have been detected, so one can suppose that SO_3 molecules simply “pushed out” Van-der-Waals gaps of graphite by lithium. After 360 h a new phase was observed at XRD-profile (Fig. 3d). Simultaneously, the interlayer distance d_{002} , as well as the TEG crystallite size changed, as shown in Fig. 4. The last one has been calculated from FWHM of (002) diffraction peak using Debye-Scherrer equation.

One can suggest that reaching steady-state corresponds to transition time of diffusion (τ). Its value according to Fig. 4 is close to 75 h. It was precisely this

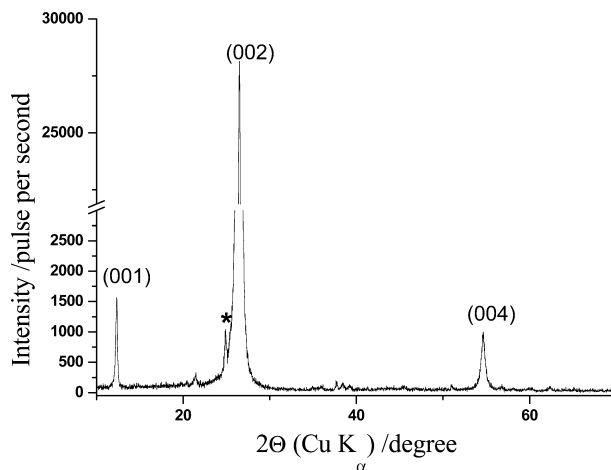


Fig. 2 XRD pattern of initial TEG sample prior to contact with lithium metal. Asterisk notes the diffraction maximum for C_3SO_3

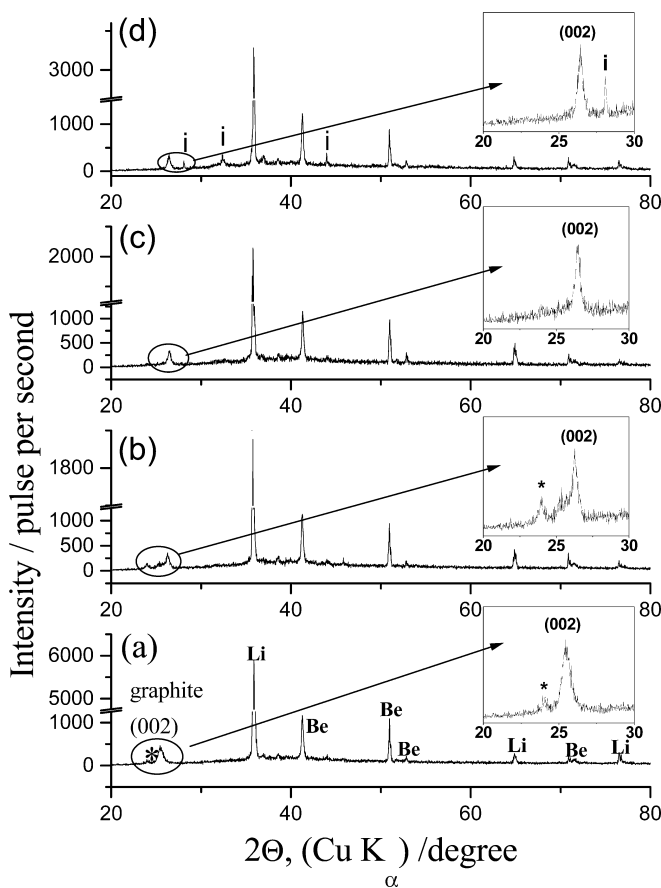
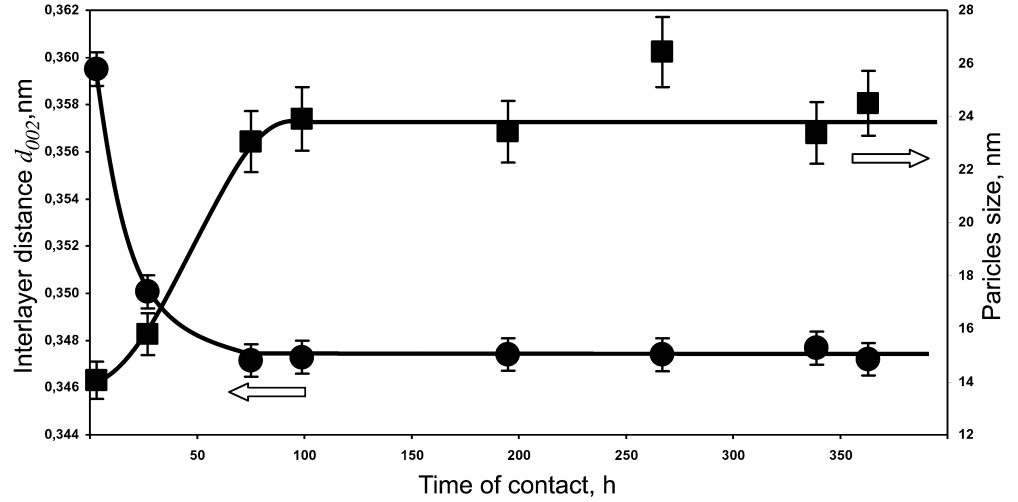


Fig. 3a–d Evolution of XRD pattern of TEG during its contact with lithium metal. Contact time: a 3 h, b 27 h, c 75 h, d 363 h

time that was necessary for the emergence of golden coloration of the frontal face of the plate. (Golden colour is known to be inherent to LiC_6). From this value and plate thickness (δ) the diffusion coefficient was estimated following equation

$$D = \delta^2 / \pi \tau \quad (1)$$

Fig. 4 Evolution of interlayer distance d_{002} (circles) and crystalline size (squares) upon contact of TEG plate with lithium



as 1.2×10^{-10} cm²/s. In principle the diffusion coefficient can be dependent on intercalation degree, i.e. index x in the formula Li_xC_6 . As noted in the Introduction, the fact of existence of such dependence was reported by many investigators; however there is great discrepancy in its nature. One way or another, the aforesaid D value must be considered as averaged.

Cathodic lithium intercalation

Figure 5 demonstrates the quasi-equilibrium dependence of the electrode potential E on lithiation degree x . Such dependence is typical for lithium intercalation into graphite. The features are more or less legible plateaus corresponding to intercalation compounds LiC_{18} , LiC_{12} , and LiC_6 .

Galvanostatic switch-on transients were registered at steady-state potential ca. 0.1 V; this potential corresponds to $x = 0.32$. The slope of quasi-equilibrium curve (dE/dx) in this case is equal to 82.5 mV.

The initial parts of switch-on transients were linear in the co-ordinates E , $t^{1/2}$ (Fig. 6). The slopes of these linear parts, as well as the interception of the Y-axis were proportional to current density (Fig. 7). Therefore, the system under study obeys the condition of plane semi-infinite diffusion, i.e. the thickness of diffusion layer was small in comparison with characteristic size of the graphite particles.

According to the theory of chronopotentiometry, concentration of diffusing species (c) at the surface in the case of linear semi-infinite diffusion obeys the following equation:

$$c = c_0 + \frac{2i\sqrt{t}}{nF\sqrt{\pi D}} \quad (2)$$

Here c_0 is concentration at the initial instant (before current switch-on), i is true current density, F is Faraday constant, n is number of electrons transferred by one diffusing species.

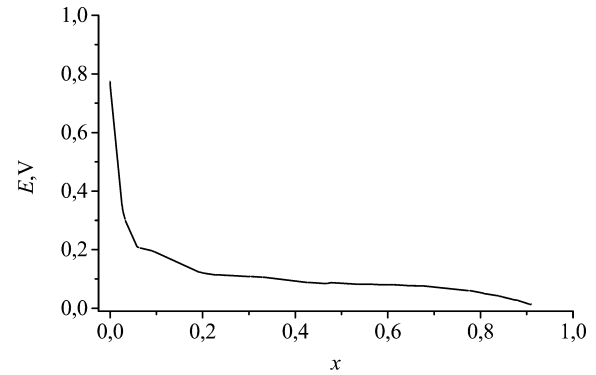


Fig. 5 "Quasi-equilibrium" curve of lithium intercalation into TEG

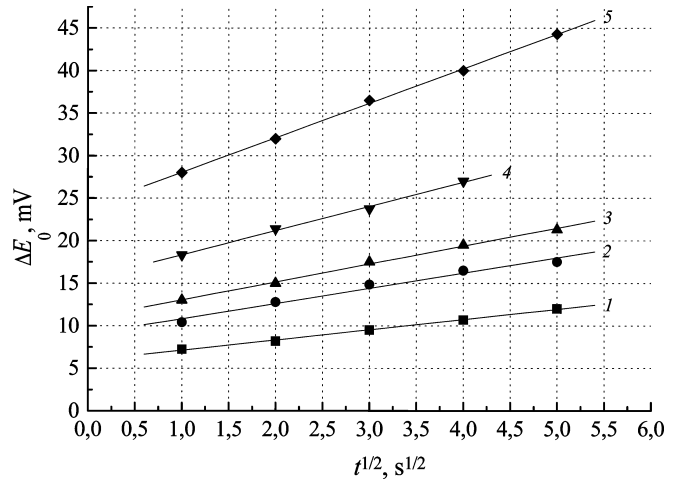


Fig. 6 Galvanostatic anodic switch-on curves in diffusion co-ordinates. Current (mA): 1 12, 2 18,3 24, 4 30, 5 42

Lithium concentration in the intercalate Li_xC_6 is connected with index x by obvious correlation:

$$c = c^*x \quad (3)$$

c^* being lithium content in LiC_6 . The density of LiC_6 can be viewed as close to that of plain graphite (about 2 g/cm³) therefore c^* is close to 0.03 mole/cm³.

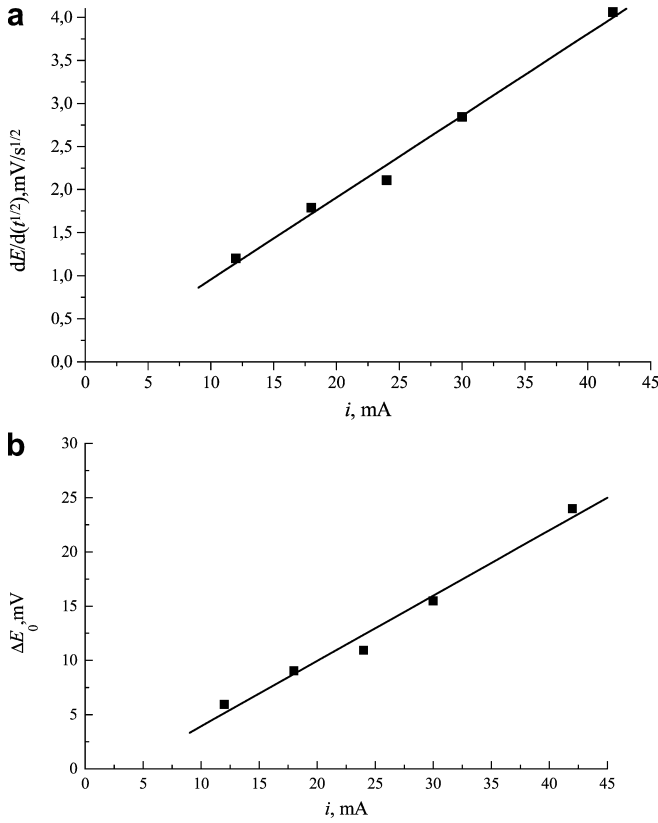


Fig. 7a, b Current dependencies of slope of switch-on curves (a) and intercept of E -axis (b)

Combination of Eq. 2 and Eq. 3 gives

$$c^* \frac{dx}{d\sqrt{t}} = \frac{2i}{nF\sqrt{\pi D}} \quad (4)$$

Variations of the potential with time are related to variations of the lithium surface concentration with time according to the following equation:

$$\frac{dE}{d\sqrt{t}} = \frac{dE/dx}{dx/d\sqrt{t}} \quad (5)$$

True current density i , i.e. current density normalized for overall internal surface of the electrode, is defined as

$$i = I/S_{sp} \cdot m \quad (6)$$

Here I is overall current, S_{sp} is specific surface area of the electrode, and m is mass of the electrode. The average diameter of fibrous particles of TEG is about 20 μ , their density is close to 2 g/cm³, therefore, S_{sp} amounts ca 1000 cm²/g. Mass of TEG (m) was 45 mg per one electrode.

From combination of Eq. 2–Eq. 6 one can obtain the following equation for calculation of the diffusion coefficient:

$$D = \frac{4}{\pi F^2 (c^*)^2 m^2 S^2} \times \frac{dE/dx}{d^2E/d\sqrt{t}di} \quad (7)$$

The slope of line in the Fig. 7a, i.e. $d^2E/d\sqrt{t}di$ is equal to 0.095 ohm/ \sqrt{s} . The diffusion coefficient, calculated according Eq. 7, proved to be close to 0.6×10^{-10} cm²/s, which barely differs from the value calculated from XRD measurements. Therefore, the nature of diffusing species is the same in the experiments with intercalation from electrolyte and at direct contact of dry graphite and lithium metal.

Knowing the value of diffusion coefficient, one can prove the suggestion about linear semi-infinite diffusion conditions. The longest time of galvanostatic experiment was 25 s, therefore the maximum thickness of diffusion layer (see Eq. 1) was about 0.7 μ , which is far less than the characteristic size of a TEG particle (20 μ). This circumstance justifies the use of Eqs. 2–6.

Conclusion

Lithium intercalation into thermoexpanded graphite (TEG) has been studied. TEG was prepared from natural graphite by treatment with sulphuric acid and subsequent heat-treatment. Lithium intercalation was studied in two different modes: (i) traditional intercalation during cathodic polarization in a liquid electrolyte, and (ii) intercalation in dry condition upon direct contact of TEG with lithium metal. The diffusion coefficient of lithium determined by both methods proved to be close to 10^{-10} cm²/s.

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