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Irreversible capacity elimination via immediate contact of carbon with lithium metal

Abstract A new method for elimination of irreversible capacity during lithium intercalation into graphite is described. The method consists of bringing the graphite electrode into tight contact with lithium metal in an electrolyte. As a result of such shorting, a passive film is formed at the graphite surface. The dynamics of the film formation and its properties depend on the correlation between the masses of lithium and graphite. The method does not result in a decrease of the reversible capacity.

Keywords Graphite · Lithium intercalation · Lithium-ion batteries · Passive films

Introduction

Graphite is known to be the most perspective and well-studied material for negative electrodes of lithium-ion batteries (see, e.g. [1, 2, 3, 4, 5]). This material possesses a rather high, close to the theoretical, specific capacity. Another advantage of graphite consists in features of its charge–discharge curves. In contrary to non-graphitized materials, the curves have prolonged plateaus at potentials close to the potential of the lithium electrode. This fact, in turn, ensures a stable and high discharge voltage for lithium-ion batteries.

The main drawback of graphite consists in so-called irreversible capacity (Q_{irr}). Graphite is characterized by a high catalytic activity, and during the first cathodic polarization of a graphite electrode in an aprotic electrolyte a number of side reactions occur at its surface.

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These reactions include electrochemical and chemical reduction of the solvent and possible reduction of anions. The reduction products contain inorganic, mainly Li_2CO_3 and LiF, as well as organic constituents. The latter can contain polymers or oligomers of alkenes, e.g. polypropylene and polyethylene in electrolytes based on propylene carbonate and ethylene carbonate, respectively. A surface layer with properties of a "solid electrolyte interface" (SEI) is formed as a result of these irreversible side reactions. Such an SEI, being an ionic conductor, prevents subsequent electrolyte and anion reductions without hindering the intercalation–deintercalation of lithium. The existence of Q_{irr} demands some extra lithium in a positive electrode, which results in a decrease of the energy density of the lithium-ion battery as a whole. It is important that Q_{irr} can be several times higher than the reversible capacity (Q_r) of the negative electrode.

Various ways for Q_{irr} elimination have been proposed, graphite surface modification and additives in the electrolytes being among them [6, 7, 8, 9, 10]. However, most of the surface modification techniques, e.g. surface oxidation, result in a decrease not only of Q_{irr} but Q_r as well [10, 11, 12, 13].

The meaning of a novel method of Q_{irr} elimination

The present work discloses a novel method for Q_{irr} elimination. The method consists of bringing the graphite electrode into tight contact with lithium metal in an electrolyte. As a result of such shorting, lithium undergoes anodic corrosion whereas cathodic processes occur at the graphite surface. These processes in fact are the same as those during the first cathodic polarization of graphite electrodes, namely electrolyte reduction with SEI formation. The dynamics of SEI formation depends on the nature of the electrolyte, the kind of graphite, the conditions of the graphite–lithium contact as well as on the balance between the masses of graphite (m_C) and lithium (m_{Li}).

During shorting, lithium is spent irreversibly for SEI formation, i.e. for Q_{irr} elimination, and reversibly for intercalation into graphite. The amount of lithium which is necessary for SEI formation ($m_{Li,1}$) is proportional to the amount of graphite:

$$m_{Li,1} = k_1 \times m_C \qquad (1)$$

The coefficient k_1 in turn is proportional to the graphite surface area; k_1 depends on the exact nature of the reduction reactions, on the conditions in which these reactions occur, and so on.

The amount of lithium which is necessary for the complete lithiation of the graphite ($m_{Li,2}$) is also proportional to m_C:

$$m_{Li,2} = k_2 \times m_C \qquad (2)$$

The coefficient k_2 reflects the intercalation capacity of the graphite. Note that the LiC_6 composition corresponds to $k_2 \approx 0.1$. Therefore the amount of lithium necessary for correct operation is governed by inequalities:

$$k_1 \times m_C \leq m_{Li} \leq k_1 \times m_C + k_2 \times m_C \qquad (3)$$

or:

$$k_1 \leq m_{Li}/m_C \leq (k_1 + k_2) \qquad (4)$$

It is obvious that if $m_{Li}/m_C < k_1$, the amount of lithium will not be sufficient for formation of a reliable SEI film and therefore for Q_{irr} elimination. If $m_{Li}/m_C > (k_1 + k_2)$, some amount of lithium will be left as non-spent even after SEI formation and complete lithiation of the graphite.

Experimental

The electrodes under study were made from natural graphite. The active mass consisted of graphite (85 w/o), acetylene black (11 w/o) and binder (4 w/o). A solution of poly(vinylidene fluoride) in N-methyl-2-pyrrolidone was used as a binder. Such a mass was subjected to homogenizing treatment in an ultrasonic dispergator (UZDN-1) and then was spread onto nickel mesh current collectors. The electrodes were dried firstly in air at 90 °C for 6 h and then in a vacuum at 130 °C for 8 h. The weight of dry active mass was 25−40 mg per electrode with a size of 15×15 mm. Then a piece of lithium foil with a thickness of 0.1 mm and known weight was tightly pressed to both surfaces of the electrode.

Electrochemical measurements were carried out in cells made from PTFE. Every cell contained one working electrode, two counter electrodes made from Li foil, and a lithium reference electrode. All electrodes were separated with porous polypropylene (PORP, Ufim, Russia). This material is analogous to the well-known Celgard. 1 M $LiPF_6$ in a mixture of propylene carbonate with diethyl carbonate (1:4) (LP-20, Merck) was used as the electrolyte. The irreversible capacity of graphite is known to be highest in electrolytes based on propylene carbonate. The moisture content of the electrolyte was not more than 50 ppm according to Fischer (K.F. titration, KF 562, Methrom).

Assembly of the cells and their filling with electrolyte were performed in a glove box with an argon atmosphere.

The potentials of the working electrodes were measured with the aid of a potentiostat (Solartron 1286 Electrochemical Interface) (it must be stressed that in the present work this instrument was used only for potential measurements, but not for controlled polarization).

Galvanostatic charge–discharge curves were registered with a multichannel computerized cycling setup, designed and made in the Institute of Problems of Chemical Physics of the Russian Academy of Sciences. The electrodes were cycled in the potential range from 0.80 to 0.02 V vs. Li^+/Li at 20 °C. In most experiments the current density was 20 mA/g of the graphite, which corresponds to 0.10–0.18 mA/cm^2 of the electrode surface.

Results and discussion

To estimate the value of the irreversible capacity, several electrodes were tested. These electrodes were as identical (the active mass from one batch, the same weight, the same manufacturing procedure, etc.) as possible. Figure 1 shows charge–discharge curves of the electrodes for the first cycle. The characteristic feature of the cathodic (charge) curves is a plateau at 0.70−0.75 V, and one or more "voltage delays", i.e. narrow and rather deep minima. The plateau is known to correspond to the aforesaid reductive processes resulting in SEI formation. The voltage delays more likely than not are related to the dynamics of SEI formation. Similar voltage delays have been noted previously [10, 14, 15]. It is worth mentioning that the irreversible capacity, specifically the difference between cathodic and anodic charges, varied over a very wide range, namely from 550 to 1150 mAh/g. Such high irreproducibility perhaps depends on delicate details of cell assembly and reflects the very complex nature of SEI-forming processes.

In spite of the large discrepancy of Q_{irr} values, the reversible capacity was more reproducible and was in the range 230–280 mAh/g.

In principle, knowing Q_{irr} values, one can calculate the coefficient k_1. Indeed, according to Faraday's law:

$$m_{Li,1} = Q_{irr} \times m_C \times A_{Li}/F \qquad (5)$$

where A_{Li} is the atomic mass of lithium.

With due account for Eq. 1, then:

$$k_1 = Q_{irr} \times A_{Li}/F \qquad (6)$$

Extreme values of Q_{irr} shown in Fig. 1, namely 550 and 1150 mAh/g, relate to k_1 values of 0.14 and 0.30, respectively.

Before shorting with lithium, graphite has a steady-state potential of ca. 3 V vs. Li^+/Li. Immediately after shorting, this potential begins to shift in a negative direction and further excursion of the potential depends on the ratio m_{Li}/m_C. Figure 2 demonstrates this evolution of the potential. Curve 1 in Fig. 2 corresponds to the situation $m_{Li}/m_C << k_1$. One hour after bringing the graphite into contact with lithium, its potential began to shift in a positive direction. The minimum in the E vs. t curve signals the instant of complete lithium exhaustion. The SEI formed in this case does not protect the graphite from side reactions; such an electrode has the same Q_{irr} as the initial one without lithium (see below). Curve 2 corresponds to the situation when m_{Li}/m_C is slightly less than k_1. In this case, an SEI with some protective power is formed but there is no lithium
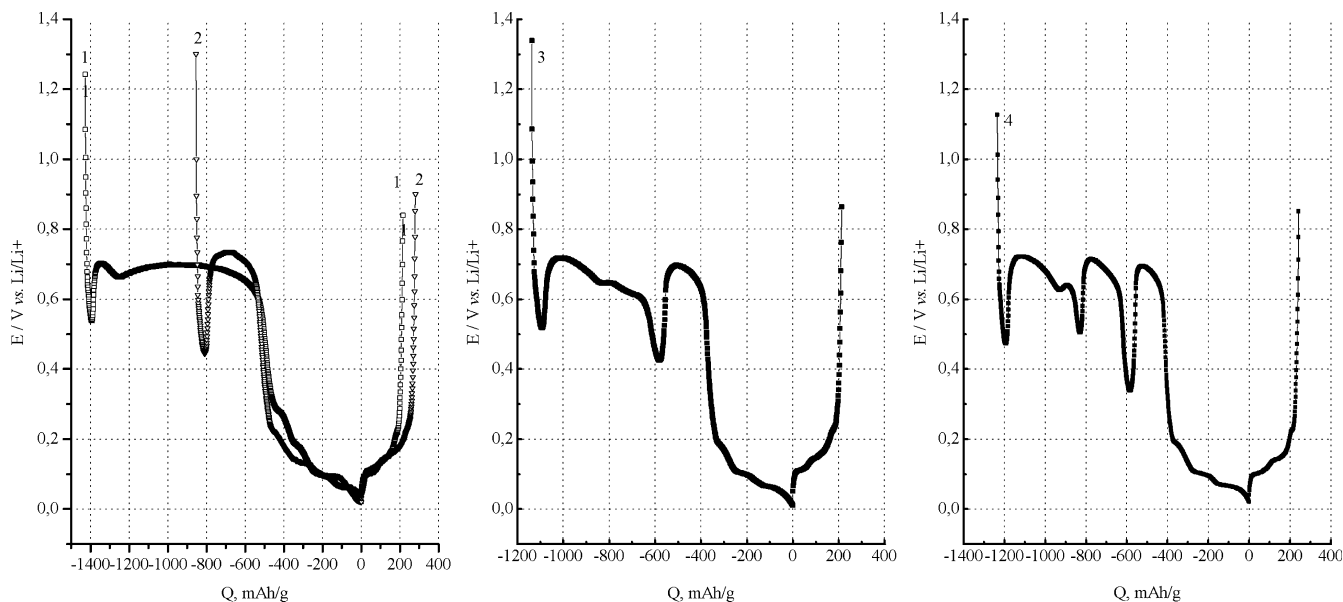
Fig. 1 Charge–discharge curves for the first cycle for graphite electrodes (samples 1, 2, 3). Current density 20 mA/g

intercalation. Curve 3 corresponds to right situation: $k_1 < m_{Li}/m_C < (k_1 + k_2)$, i.e. formation of a good protective SEI along with partial graphite lithiation. In this case, 4–5 h after contact of graphite with lithium, the potential approached 110 mV and then it was invariant for 25–35 h. A slight potential shift in the positive direction in this time period can be explained by corrosion, i.e. lithium deintercalation with simultaneous slow
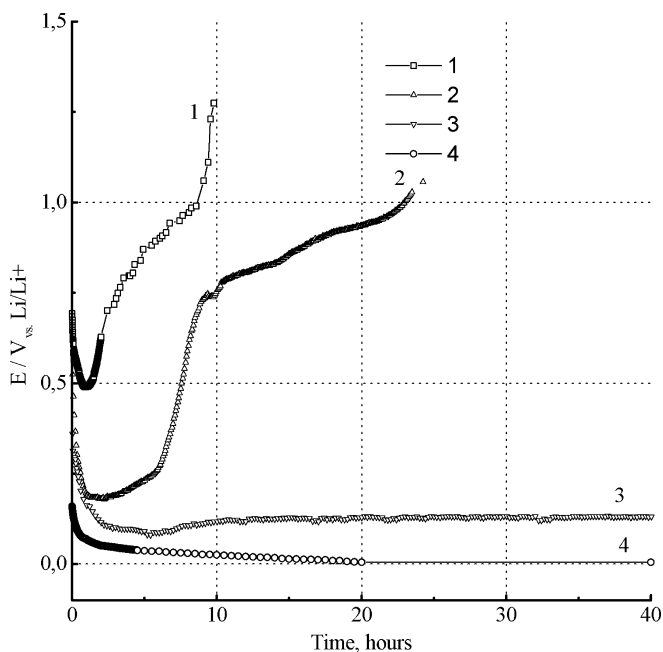

Fig. 2 Potential vs. time for graphite electrodes after shorting with lithium metal with various m_{Li}/m_C values: *1*, 0.046; *2*, 0.11; *3*, 0.22; *4*, 0.36

electrolyte reduction. It was a process of electrode self-discharge. Finally, curve 4 corresponds to the situation $m_{Li}/m_C > (k_1 + k_2)$. In this case, immediately after contact of graphite with lithium a cathodic process occurred with a rather high rate: after 2 h the potential was 50 mV. Then the rate of potential shift decreased and after 24 h the potential was close to that of the lithium electrode and did not change for 25 h. The constancy of the potential bore testimony to the presence of non-spent lithium at the electrode surface.

Figures 3, 4, 5 demonstrate charge–discharge curves for electrodes with different m_{Li}/m_C values. All these experiments were begun not less than 24 h after bringing the electrodes into contact with lithium.
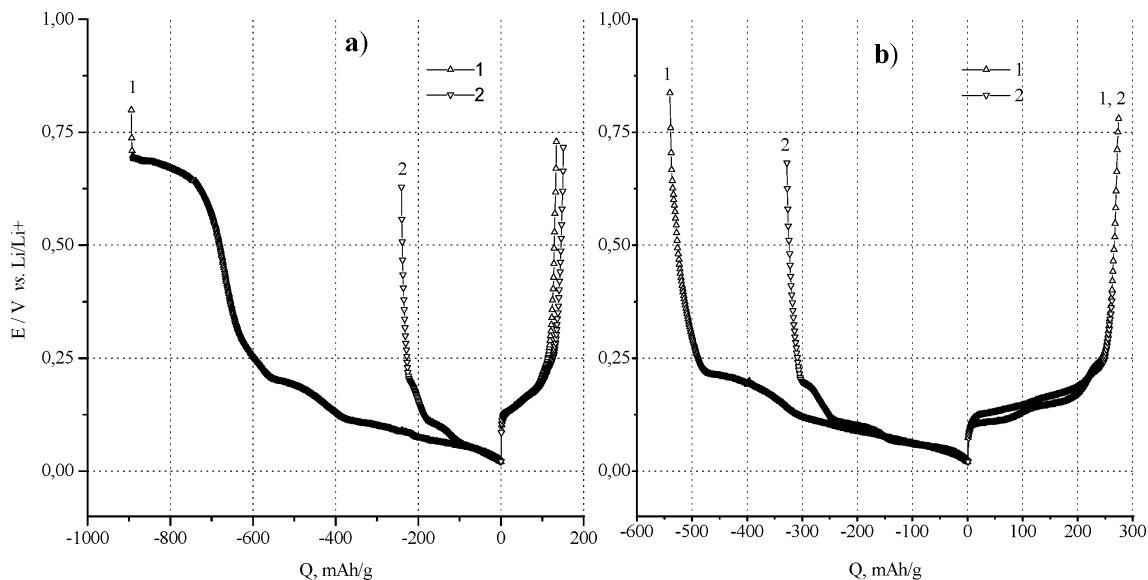
Charge–discharge curves for electrodes with low values of the parameter m_{Li}/m_C are shown in Fig. 3. One can see that the irreversible capacity of the electrode with $m_{Li}/m_C = 0.046$ did not decrease (Fig. 3a). True enough, the initial voltage delay disappeared in this case. As to reversible capacity, it even decreased in comparison with the initial untreated graphite.

The reason for such Q_r diminution can be a feature of the passive film formed under these conditions. In this case, i.e. with a low value of the parameter m_{Li}/m_C, the passive film was formed at potentials in the range 0.8–0.4 V. It has been shown [16] that properties of passive films depend on the potential of their formation: at rather positive potentials (e.g. more positive than 0.4 V), loose films with high resistance ("bad" films) are formed, whereas at more negative potentials, dense films with low resistance ("good" films) can be formed. Diminished values of Q_r as well as high polarization during anodic discharge can be easily explained, providing the high ohmic resistance of the passive film and the very weak dependence of the potential on the lithiating degree intrinsic for graphite.

Irreversible capacity of the electrode with $m_{Li}/m_C = 0.11$ decreased up to 265 mAh/g. Such a decrease
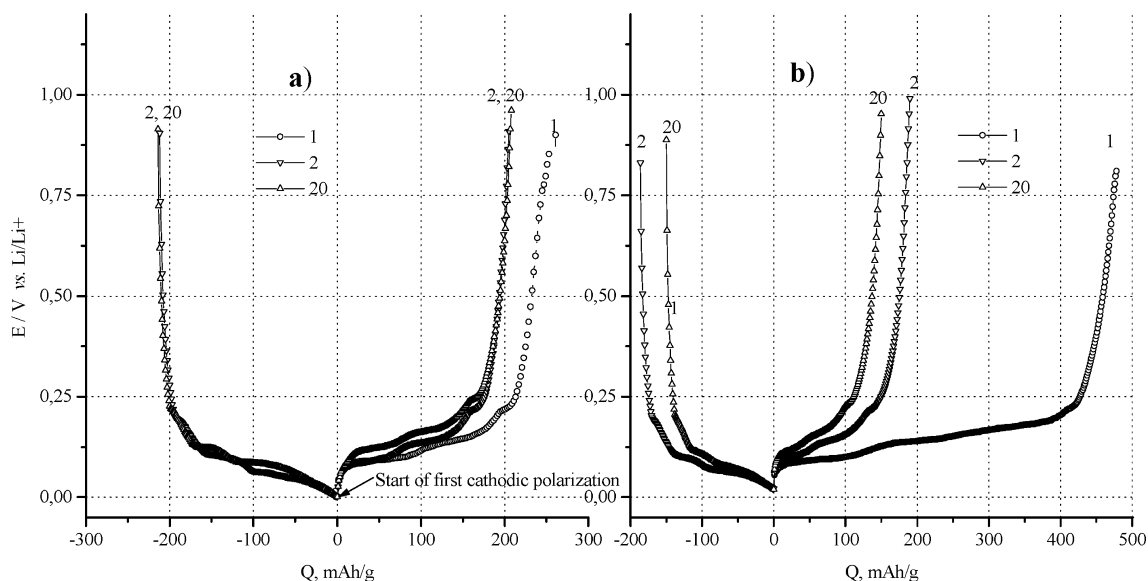
Fig. 3 Charge–discharge curves for graphite electrodes with various m_{Li}/m_C values: (**a**) 0.046; (**b**) 0.11. Cycle numbers are near the curves

of Q_{irr} points to formation of some passive film with the properties of a solid electrolyte. The reversible capacity in this case amounted to 280 mAh/g.

Figure 4 exemplifies charge–discharge curves for electrodes with high values of the parameter m_{Li}/m_C, specifically 0.28 and 0.36. In these cases, "good" passive films were formed but some excess of lithium remained at the electrodes. This extra lithium was dissolved during the first anodic run (see, especially, Fig. 4b). During the following cycling the irreversible capacity was
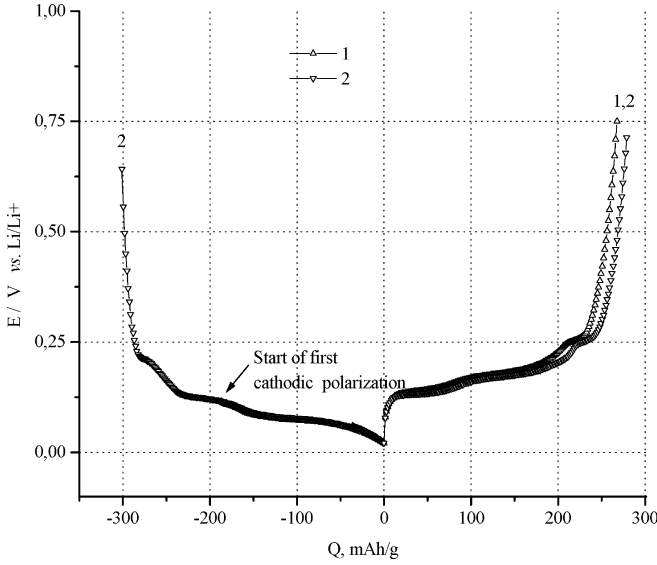
absent, but reversible capacity was somewhat lowered. The exact reason for such a diminution of Q_r is still unclear.

Finally, Fig. 5 shows charge–discharge curves for the electrode with the proper correlation $m_{Li}/m_C = 0.22$. In this case the amount of lithium was sufficient for the formation of a "good" dense passive film with high ionic conductivity as well as for partial lithiation of the graphite. The cathodic run in this case was started with the potential at 130 mV, corresponding to the degree of lithiation. During the following cycling the irreversible capacity amounted to 290 mAh/g, intrinsic to this kind of graphite at the specified current density.

In the general case the amount of lithium brought into contact with a graphite electrode can be expressed in electric units (according to Faraday's law) as a sum of three items:
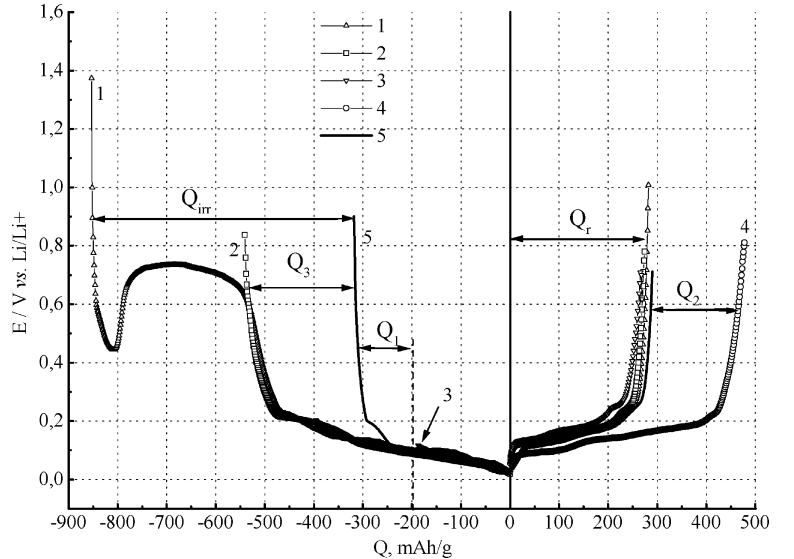
$$Q = Q_0 + Q_1 + Q_2 \tag{7}$$

Fig. 4 Charge–discharge curves for graphite electrodes with various m_{Li}/m_C values: (**a**) 0.028; (**b**) 0.36. Cycle numbers are near the curves

Fig. 5 Charge–discharge curves for graphite electrodes with $m_{Li}/m_C = 0.22$. Cycle numbers are near the curves

Table 1 Values of the parameters Q, Q_1, Q_2, Q_3, Q_{irr} and k_1

m_{Li}/m_C	Q (mAh/g)	Q_1 (mAh/g)	Q_2 (mAh/g)	Q_3 (mAh/g)	Q_{irr} (mAh/g)	K_1
0.046	180	0	0	760	940	0.24
0.11	420	0	0	265	685	0.18
0.22	840	100	0	0	740	0.19
0.28	1070	200	50	0	820	0.21
0.36	1380	200	250	0	930	0.24

Q_2, Q_3, Q_{irr}, Q, and k_1 for the experiments of the present work are presented in Table 1 (the coefficient k_1 was calculated with Eq. 6).

It is of much interest and importance whether the direct contact of graphite with lithium results in degradation of the electrode performance upon prolonged cycling. Such prolonged tests were performed with two plain graphite electrodes and with two electrodes after contact with lithium. The parameter m_{Li}/m_C in the latter case was equal to 0.11 and 0.22. The results are presented in Fig. 7. One can see that the tendency to degradation of the graphite electrodes after contact with lithium was not more than that of plain graphite electrodes, at least during 50 cycles with a current density of 20 mA/g.

Graphite with pressed-on lithium makes a short-circuit galvanic couple. In principle, a plain graphite electrode can be shorted with a lithium electrode via an external circuit. Such an experiment was carried out and Fig. 8 shows evolution of the potential of this electrode during shorting and after circuit opening. One can see that just after closing the circuit the potential dropped to 0.0 V vs. Li^+/Li, but after circuit opening the potential very soon approached its initial value. This phenomenon can be explained as follows. The contact of the graphite active mass with the nickel current collector is much better than that with lithium foil pressed onto the electrode surface. In result the current in an external short

where Q_0 is the charge spent in passive film forming, Q_1 is the charge spent in lithium intercalation into graphite, and Q_2 is the charge corresponding to the excess amount of lithium. It must be stressed that the quantities Q_1 and Q_2 exist only at rather high values of the parameter m_{Li}/m_C, otherwise $Q_1 = Q_2 = 0$. Charge–discharge curves for the first and second cycles give a possibility to calculate Q_1, Q_2, the non-compensated irreversible capacity Q_3 (in the case of an insufficient amount of lithium), and the reversible capacity. The true value of Q_{irr} can be calculated with:

$$Q_{irr} = Q_0 + Q_3 = Q - Q_1 - Q_2 + Q_3 \qquad (8)$$

Figure 6 shows a schematic diagram of the mutual correlation between Q_1, Q_2, Q_3, and Q. Values for Q_1,

Fig. 6 Illustration for Table 1. *1–4* are charge–discharge curves for the first cycle: *1*, initial graphite; *2*, graphite after contact with lithium metal with $m_{Li}/m_C = 0.11$; *3*, graphite after contact with lithium metal with $m_{Li}/m_C = 0.22$; the *dashed line* marks the start of the first cathodic polarization; *4*, graphite after contact with lithium metal with $m_{Li}/m_C = 0.36$; *5*, charge–discharge curves for the second cycle
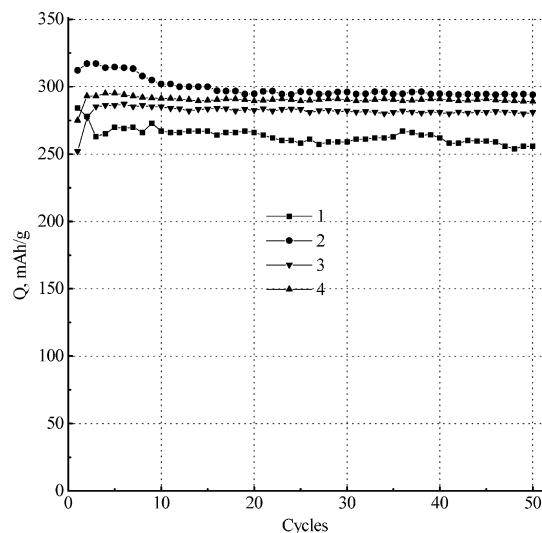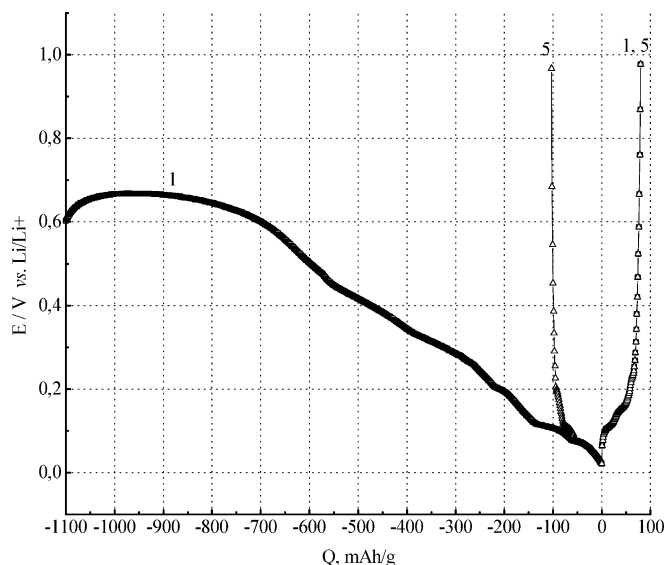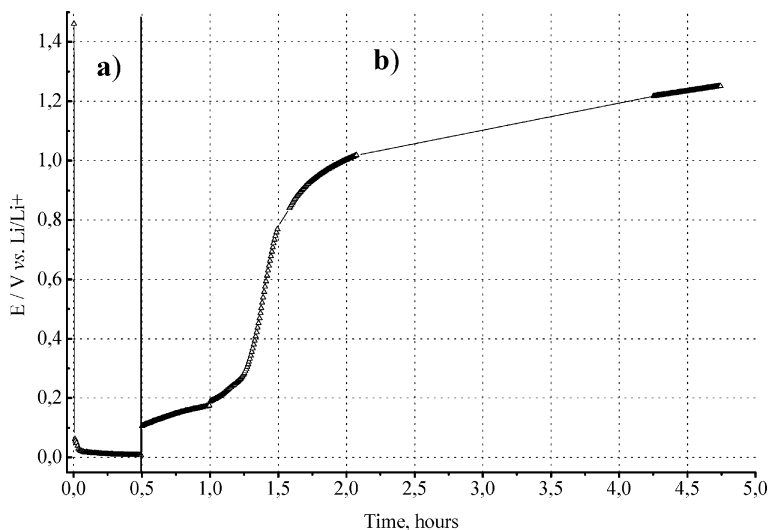
Fig. 7 Capacity fading of graphite electrodes during cycling in LP-20: *1*, *2*, initial graphite; *3*, graphite after contact with lithium metal with $m_{Li}/m_C = 0.11$; *4*, graphite after contact with lithium metal with $m_{Li}/m_C = 0.22$

Fig. 9 Charge–discharge curves for graphite electrodes after shorting with lithium metal via an external circuit. The cycle numbers are near the curves

circuit made from graphite and lithium electrodes was higher than the short-circuit current in the case of pressing a piece of lithium onto the electrode surface. The current distribution over the volume of the graphite electrode with external shorting was much more uneven than for the electrode with pressed-on lithium, and the passive film at the former electrode had poor protective properties. The charge–discharge curves testify in favour of such an explanation in a roundabout way. These curves are shown in Fig. 9. It is seen that the irreversible capacity in this case did not decrease, and the reversible capacity amounted only to 80 mAh/g. Such a low reversible capacity can be explained by destruction of the electrode structure due to passing of a high short-circuit current. Indeed, in the course of cell disassembly, disruption of the electrode was noted.

Conclusion

Thus, a novel method for irreversible capacity elimination is proposed. The method consists in bringing a graphite electrode into tight contact with lithium metal in an electrolyte. Such a technique either wholly or partially eliminates the irreversible capacity without decreasing the reversible capacity. The degree of irreversible capacity decrease depends on the parameter m_{Li}/m_C. From the results obtained one can conclude that the properties of passive films depend on the potential of their formation: at rather positive potentials (e.g. more positive than 0.4 V), loose films with a high resistance ("bad" films) are formed, whereas at more negative potentials, dense films with low resistance ("good" films) can be formed. Such a

Fig. 8 Potential vs. time for graphite electrodes after (**a**) shorting with lithium metal via an external circuit and (**b**) circuit opening

"good" film, being an ionic conductor, prevents subsequent electrolyte and anion reduction without hindering the intercalation–deintercalation of lithium.

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