Lithiated Graphite Materials for Negative Electrodes of Lithium-Ion Batteries

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For the first time an attempt was made to eliminate problems of irreversible charging in the first cycle when a new lithium-ion battery is set to work. The research work was based on an artificial lithiation of the carbonaceous anode via three lithiation techniques: the direct electrochemical method, lithiation using $FeCl_3$ as mediator, and via a direct contact with metallic Li. The cycling ability and specific capacity were the criteria of suitability, the contact with metal lithium was found to be the most efficient one. The battery grade carbon and/or expanded graphite were used as anode materials.

Keywords: lithium, graphite, irreversible capacity, battery, electrode.

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1. INTRODUCTION

The capacity losses in initial charge-discharge cycles, which arise on a negative electrode, are caused by the irreversible capacity of graphite. During the first formatting cycle, the potential capacity of a lithium-ion battery is reduced from 15% up to 45%. These losses depend on the formation of a Solid Electrolyte Interface (SEI) thin film on the solid-liquid electrode interface. During the first charging the redox reactions between lithium cations (Li+) and molecules of a solvent occur. These reactions proceed on the electrode surface, and the magnitude of losses depends on the specific surface area of the graphite material. The SEI layer is composed of the products of redox reactions, for example, Li_2CO_3, LiO_2, C_2H_4, CO_3^{2-}, $LiCH_3$, and other inorganic or organic molecules. The exact composition of the SEI layer depends on the kinds of solvents used, the mixture of dimethyl carbonate (DMC) and ethylene carbonate (EC) being the most usual. The lithium salt $LiPF_6$ was added to DMC/EC mixture to obtain the 1 mole electrolyte, this electrolyte was used in our experiments. The SEI layer has a specific conductive property: it works as membrane that is transparent for Li atoms but nonconductive for electrons. This characteristic property of the SEI layer ensures the lithium-ion battery a very low self-discharge rate. In our research, two types of the crystalline graphite, natural and expanded, have been used. Their main properties are described in Table 1. These two graphite types represent the most widely used materials for the negative electrode in lithium-ion batteries. Our idea has been to prepare a graphite electrode that already contains Li atoms before the first charging cycle. These Li atoms can be used in the formation of the SEI layer. The entire capacity of the positive electrode is preserved and its Li atoms can be used for the charge transfer [1–5].

Table 1. The basic parameters of graphite materials.

Type	Particle Diameter [μm]	Specific Surface [$m^2 \cdot g^{-1}$]	Sheet Distances [nm]
Natural	< 11	10	0.336
Expanded	< 150	68	1.2

2. EXPERIMENTAL WORK

2.1. Materials and procedures

Three different lithiation methods (*A*, *B* and *C*) are described further in this paper. Method *A* represents chemical redox process of inorganic compound *n*-butyllithium and graphite. The *n*-butyllithium acts as lithium donator for graphite structure. Method *B* builds on method *A*, it use iron (III) chloride as a catalyst that improves a transfer process of lithium atom between *n*-butyllithium and graphite. In contrast to methods *A* and *B* the method *C* represents electrochemical process, where the lithiation transfer is ensured by open-circle potential of the half cell. This potential effects constrained transport of lithium atoms to graphite structure. All these methods should provide prelithiated graphite material which can be used as the precursor for preparing of electrodes. The first part deals with the use of *n*-butyllithium as donor of Li atoms. The measurements showed that *n*-butyllithium is able to hand over the Li atoms to graphite material, i.e., to insert Li atoms between graphite sheets. The second part of research is based on the results obtained during the first part. In second part of experiment the ionic compound $FeCl_3$ was used to support the insertion of lithium. According to our assumption of the reaction *n*-butyllithium and graphite, the ionic molecule had to tear off the Li atom from the butyl chain. The separated Li atom could be easier inserted into or bonded to the graphite structure. The third part is a description of a special lithiation process based on the conductive connection between the graphite electrode and the metallic Li. If is the graphite electrode is dipped in an aprotic electrolyte together with the metallic Li, then we get the half-cell with the electrochemical potential of approximately 2.5V. Thus prepared half-cell can be short-circuited via an outer conductor; in this case, the electric current begins to flow through the conductor. When the electrode steps into the reduction reaction between Li cations and electrons on the graphite; we call this process an electroless lithiation [6–9].

2.2. Process of lithiation

This paragraph describes the steps of usage of the lithiated graphite. All steps were carried out under the inert argon atmosphere. The solution of *n*-butyllithium contained 2.5 molar concentration of *n*-butyllithium dissolved in *n*-hexane. The Li salt solution of 1 molar concentration of $LiPF_6$ [10, 11] was used in procedures *B* and *C* described next in the paper.

A. Steps of lithiation with n-butyllithium.

1. Graphite material was dried at the temperature of 150°C for 12 hours in a vacuum chamber to remove the residual moisture from graphite.
2. Then *n*-butyllithium was added into graphite in the molar ratio; it corresponded to one Li atom per six carbon atoms and resulted in the formation of LiC_6.
3. Next, the mixture of *n*-butyllithium and graphite was stirred for 24 hours under room temperature.
4. Then the mixture was filtered. The lithiated graphite blend, which we got, was purged by the *n*-hexane solvent in order to remove *n*-butyllithium residues from it. The mixture was stirred with *n*-hexane for 6 hours. After the purging step, the mixture was filtered again.
5. After filtering, the lithiated graphite should be in its final state (as precursor for preparing the testing electrode), without any residues.

During this experiment, an unexpected event happened – an exothermic reaction while synthesizing graphite and *n*-butyllithium. That reaction was accompanied by the formation of a gas and, as a result, there was initiated an explosion in the glove box. We assume it could be caused by the reaction of the remaining humidity in graphite and *n*-butyllithium. Therefore, to avoid this trouble, it is necessary to dry the graphite precursor from the residual water.

B. Steps of lithiation with n-butyllithium and iron (III) chloride ($FeCl_3$).

1. The graphite material was dried at the temperature of 150°C for 12 hours in a vacuum chamber.
2. The $FeCl_3$ compound was also dried in a vacuum chamber at the temperature of 150°C but for 24 hours. It is very important to remove the residual moisture from $FeCl_3$ powder.
3. Then, both dried components (graphite and $FeCl_3$) were mixed together in the ratios calculated in relation to the hexagonal unit (C_6) of graphite per one $FeCl_3$ molecule. The two prepared ratios of the components were: (a) ten carbon atoms per one $FeCl_3$, molecule, ratio 10:1; and (b) six carbon atoms per one $FeCl_3$, molecule, ratio 6:1. Each composition of two ratios was being stirred with *n*-hexane for 24 hours, thus making the compositions more homogeneous.
4. Next, the mixture was filtered and dried in order to remove *n*-hexane.
5. After that, *n*-butyllithium was added into the mixture. The molar ratio was calculated as one Li atom per six carbon atoms – LiC_6.
6. At the end, the steps like those in Section *A* (steps no. 4 to 5) followed.

C. Electroless lithiation.

1. Graphite material was dried at the temperature of 150°C for 12 hours in a vacuum chamber.
2. To the graphite material 10 wt% of binder (polyvinylidenefluoride – PVDF) was added so as to improve the material properties, and a negative electrode was prepared from the dried graphite material.
3. The electrode material was coated onto the cooper foil (thickness 35 µm) and then sintered at the temperature of 50°C for 24 hours.
4. Next, the prepared electrode was connected to the system shown in Fig. 7. During this step, the electrode material was being reduced by Li ions for 48 hours, from potential 2.5V to 100 mV.
5. In the last stage of this process, the electrode material was stripped off from the cooper collector and dried out under room temperature. That lithiated material was used as precursor for preparing the testing electrode.

3. EXPERIMENTS AND RESULTS

3.1. Graphite lithiation with n-butyllithium

Here we describe manufacturing of the negative electrode from the pre-lithiated graphite. The pre-lithiated graphite material was obtained as described in Section *A. Steps of lithiation with n-butyllithium*. Through the manufacturing steps, we have obtained the lithiated graphite material in a powder form. The lithiated graphite powder was mixed with the PVDF

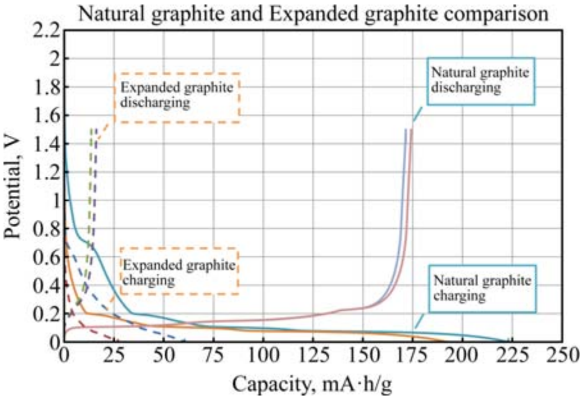

Fig. 1. Charge-discharge capacity characteristics of natural graphite COND 5995 and expanded graphite by Bochemie a.s.

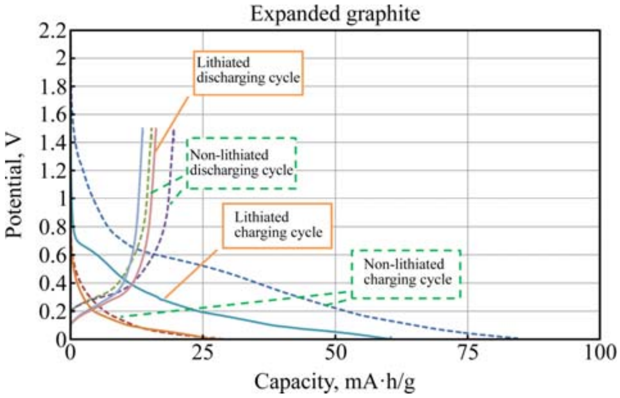

Fig. 2. Charge-discharge characteristics of expanded graphite (by Bochemie a.s.) without lithiation treatment.

binder. The binder was calculated as 10 wt% of the lithiated graphite material and it had to be dissolved in the *N*-methyl-2-pyrrolidone (NMP) solvent. The electrode mixture was stirred for 24 hours, then the mixture was deposited on the cooper foil (thickness 35 μm). The wet thickness of the coating layer was 80 μm. After that, the coating mixture was sintered for 12 hours at the temperature of 50°C. Similar to the final step of the electrode manufacturing process described above, small rounded electrodes with the diameter of 18 mm were cut off. Those electrodes were subject to the pressure of 2 tons per cm^2. The electrodes were subsequently measured on a potentiostat/galvanostat in the half-cell system. The arrangement of electrodes was as follows: the working electrode (WE) was connected to the analysed electrode and metallic Li served as the counter electrode (CE). At the beginning of our experiments, two types of graphite were measured and compared (see Fig. 1). The graph in Fig. 2 shows the measured characteristics of the expanded graphite, illustrating the comparison of the characteristics of the lithiated and non-lithiated materials. The electrode made from the non-lithiated material (dashed curve) had the capacity of about 20% higher than that from the lithiated one (solid line).

The graph in Fig. 3 shows the measured characteristics of the natural graphite. The electrode made from the non-lithiated material (dashed curve) has a higher capacity than that from the lithiated one (solid line), as in the previous case. Natural graphite did not show the difference of capacity as big as in the case of the expanded graphite [12, 6].

Both types of graphite electrodes (lithiated and non-lithiated) demonstrated an approximately similar irreversible capacity. The non-lithiated natural graphite material has the irreversible capacity around 24% and the lithiated natural graphite has the irreversible capacity around 23% (see Fig. 3). A more noticeable difference is in the case of the expanded graphite (Fig. 2). The non-lithiated electrode material has the irreversible capacity around 82% and the lithiated one – around 77%. The summarized results of lithiation (*A. Steps of lithiation with n-butyllithium*) are listed in Table 2. There LITHI means the lithiated graphite material and NON LI means the initial graphite material without any Li atoms.

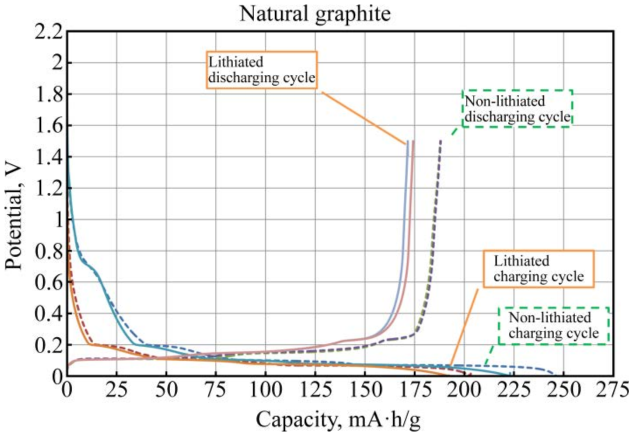

Fig. 3. Charge-discharge characteristics of natural graphite (COND 5995) without lithiation treatment.

Table 2. Properties of lithiated graphite materials

Type	Stabilized Capacity [mA·h/g]		Irreversible Capacity [%]	
	LITHI.	NON LI.	LITHI.	NON LI.
Natural	188	203	23	24
Expanded	27	28	77	82

3.2. Graphite doped by iron (III) chloride ($FeCl_3$)

The experiments discussed in this Section are based on the results from Section *3.1. Graphite lithiation with n-butyllithium*. From Table 2 it is clear that the expanded graphite has poor capacity characteristics. Based on these results, had been proceed to advanced lithiation process. Following experiments was carried out with natural graphite CR 5995. In terms of irreversible capacity, only slight difference between lithiated and non-lithiated graphite material was observed. There is a missing intercalation reaction between *n*-butyllithium reagent and graphite material.

In the other experiments was used ionic compound, iron (III) chloride ($FeCl_3$). $FeCl_3$ belongs to halides group, halides are binary compounds, of which one part is a halogen atom and the other part is an element which is more electropositive. The halide group contains these significant compounds copper (II) chloride ($CuCl_2$), manganese (II) chloride ($MnCl_2$) and cobalt (II) chloride ($CoCl_2$). All of these compounds are suitable for using in lithiation process. Was decided to use $FeCl_3$ due to its three chloride atoms which cause partial distribution of charge. The electrode material, its manufacturing process is described in part *B*, was coated on cooper foil with addition of binder. The manufacturing process of electrodes is the same as in previous case, which is described in paragraph 3.1 above. The electrodes were subsequently measured on potentiostat/galvanostat instrument (Bio-Logic) in a half-cell system. The measured characteristics are displayed in Figs. 4 and 5 [8, 12].

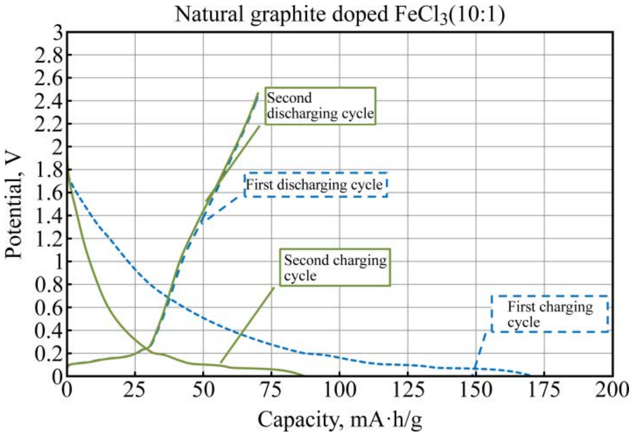

Fig. 4. Charge-discharge characteristics, graphite doped by $FeCl_3$ in the ratio 10:1.

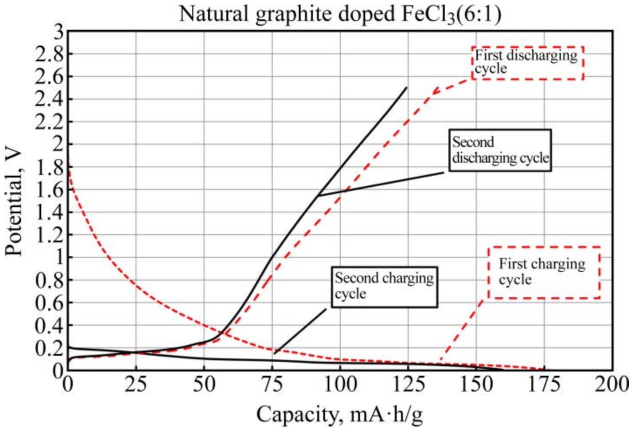

Fig. 5. Charge-discharge characteristics, graphite doped by $FeCl_3$ in the ratio 6:1.

The obtained results show the capacity characteristics of measured specimens. The electrode material with ratio 10:1 (ten carbon atoms per one atom of $FeCl_3$) has lower stable capacity (around 85 mA·h/g) and higher irreversible capacity (58%) than electrode material with ratio 6:1, see Fig. 4. The material with the ratio 6:1 has the stable capacity around 160 mA·h/g and the irreversible capacity 15%, see Fig. 4. This marked difference of material characteristics is evident from Fig. 6 and Table 3.

The differences of capacity characteristics are displayed in Fig. 6. Measured results of that experiment are given in Table 3 and Table 4.

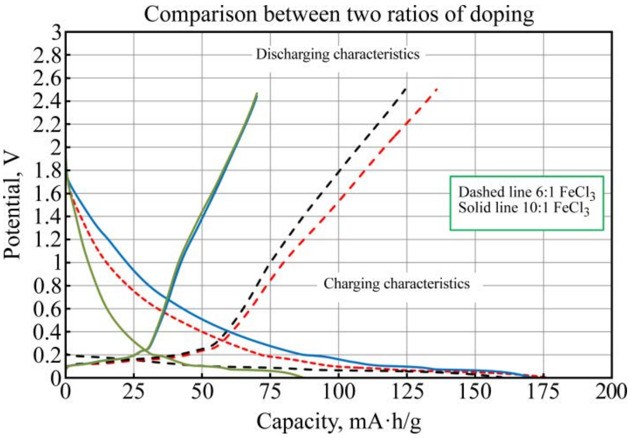

Fig. 6. Comparison between two ratios of $FeCl_3$.

Table 3. Obtained values of irreversible and steady capacity

Ratio of $FeCl_3$	Permanent Capacity [mA·h/g]	Irreversible Capacity [%]
10:1	87	58
6:1	162	15

Table 4. Conclusion summary

Type	Stable Capacity [mA·h/g]	Irreversible Capacity [%]
Non-treated	203	24
Lithiated	188	23
Doped $FeCl_3$ (10:1)	87	58
Doped $FeCl_3$ (6:1)	162	15
Electroless lithiation	**210**	**2**

3.3. Electroless lithiation process

The previous experiments (Sections 3.1 and 3.2) give only small improving of the irreversible capacity and of the characteristics of materials. There is only negligible improvement of an irreversible capacity along with the decrease of the steady material capacity. This Section considers a simple lithiation method based on the potential of electrochemical cell. The electrochemical potential is formed between the graphite electrode (material based on graphite with additives deposited on the copper collector) and the electrode from metallic Li [9, 13, 14]. This half-cell is connected through a wire that serves as an outer conductor of electrons, which system it sketched in Fig. 7. The system in Fig. 7 was used for the manufacturing of the electrode material. As an electrolyte, 1M concentration of $LiClO_4$ salt (dissolved in the mixture of DMC and EC) was used. This process is described in Section *C, 2.1*. The material thus prepared was deposited on the electrode collector through the steps described in *C*. The capacity characteristics of the pre-lithiated graphite are shown in Fig. 8.

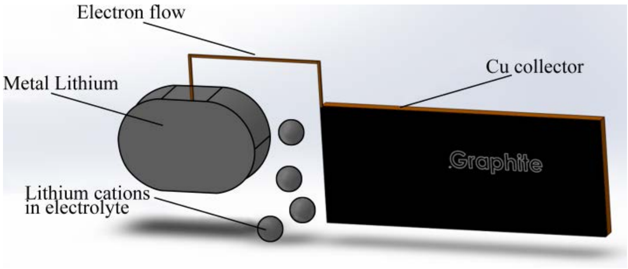

Fig. 7. Conception of electroless lithiation system.

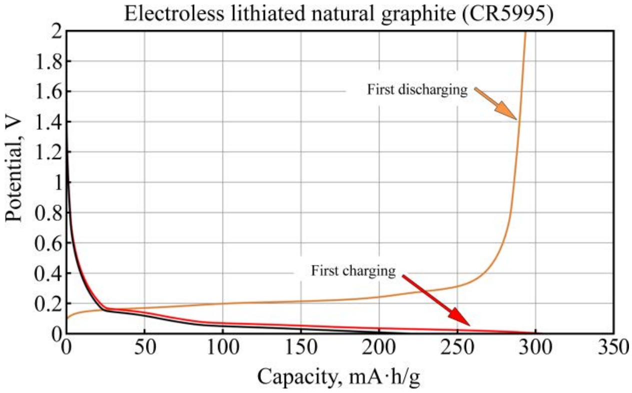

Fig. 8. Capacity characteristics of pre-lithiated natural graphite (COND CR 5995).

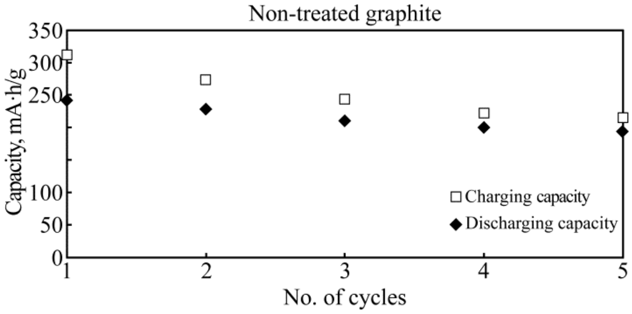

Fig. 9. Capacity characteristics of initial (pure) natural graphite.

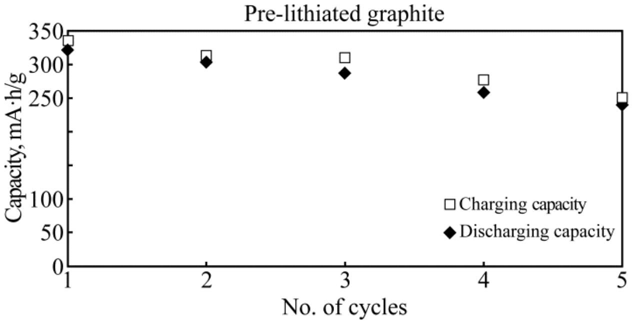

Fig. 10. Capacity characteristics of lithiated natural graphite material.

The values of the irreversible capacity and steady capacity, which were measured through the electroless lithiation process, showed a significant improvement of the characteristics just mentioned. This lithiation process fully saturated the graphite structure by Li atoms. These atoms are used during electrode formatting (they are consumed to creation SEI layer on heterogeneous interphase electrode/electrolyte), also they preparing the positions inside the graphite structure for the other Li atoms in the following charge-discharge cycles.

In Figs. 9 and 10 is shown the comparison of natural graphite capacity characteristics. Figure 9 shows non-treated natural graphite capacity during 5 cycles, the Fig. 10 shows the same material treated by pre-lithiation process.

4. CONCLUSIONS

In the first part of our experimental work (*3.1 Graphite lithiation with n-butyllithium*) the lithiation process with *n*-butyllithium reagent is described. In experiments we used two kinds of graphite: expanded and natural one (more in Table 1). Figures 2 and 3 show the comparison between lithiated and non-lithiated materials. Low capacity characteristics of expanded graphite may be caused by the distance extension of graphene sheets with the following exfoliation, which occurred during lithiation. The natural graphite does not show this pronounced difference in capacity characteristics. The irreversible capacity of natural graphite slightly improved – from 24% to 23%. *N*-butyllithium is a too feeble reduction agent for graphite. The atoms of Li+ are not able to leave the *n*-butyl chain and get the intercalation to graphite.

The second part of our work (*3.2 Graphite doped by iron (III) chloride ($FeCl_3$)*) uses the iron (III) chloride ionic compound and shows a higher irreversible capacity suppression. The obtained results are listed in Table 3, which says that the most suitable ratio of iron (III) chloride is 1:6, i.e. one molecule of $FeCl_3$ per six carbon atoms (similar to the non-stoichiometric compound LiC_6). The experiment with the ionic compound resulted in a decrease of the irreversible capacity from 24% to 15%. The last part of our work (*3.3 Electroless lithiation*) brought the expected results, reflected in Fig. 8. The irreversible capacity of natural graphite decreased from 24% to 2%.The overall results are summarized and compared in Table 4. Our experiments confirm that the idea to diminish the irreversible capacity by using pre-lithiated graphite material is workable. The electroless lithiation method used for preparing of a pre-lithiated electrode material is a theme for futher discussions. Its utilization and commercialization could be difficult but it can bring about higher capacities and better characteristics of lithium-ion batteries.

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Реферат

Впервые была предпринята попытка устранить проблемы необратимой зарядки в первом цикле, когда новый литий-ионный аккумулятор устанавливается в рабочем режиме. Основой исследования послужило искусственное легирование углеродистого анода с использованием трех методов легирования: прямой электрохимический метод, легирование с помощью $FeCl_3$ как переносчика, и при непосредственном контакте с металлическим Li. Критериями эффективности были: возможность циклических изменений и удельная производительность, для которых контакт с металлическим литием оказался наиболее эффективным способом. В качестве материала для анода аккумулятора использовали углеродистую сталь и/или вспученный графит.

Ключевые слова: литий, графит, необратимая емкость, батарея, электроды.