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Reduction of Irreversible Capacity in Lithium-ion Batteries

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Abstract. This article is focused on a research of negative materials for Lithium-ion batteries. In the research are considered methods, which can lead to enhance capacity of Lithium-ion batteries. The increase of the battery capacity is based on reduction of irreversible capacity. The majority of Li-ion batteries which are used in this time has negative electrode make from graphite. On interface between electrolyte and graphite electrode originates the SEI layer (Solid-Electrolyte Interphase), this layer is the cause of irreversible capacity of graphite. This layer is indispensable for appropriate battery function but for creating this layer is consumed almost one-third potential capacity of Li-ion cell. In our research we attempted to prepare the material which would reduce these capacity losses. Was designed a concept where n-butyllithium (C_4H_9Li) reagent behaves as the source of lithium atoms and graphite acts like acceptor of lithium atoms. This process is called „lithiation“, our conception presents n-butyllithium like oxidative reagent which is able to reduce graphite material by Li atoms. Lithium atoms are intercalated between graphite sheets (as at charging process), resulting of this process is new lithiated electrode material which can be used for prepare of negative electrode for Li-ion cells.

Key words

Graphite, Lithium, Battery, Capacity, Butyllithium, Iron(III) chloride

1. Introduction

The losses arise on the negative electrode, between the first and second charge – discharge cycle. At charging process, on the electrode interface occurs to reduction Li^+ cations and another redox processes with electrolyte solvents molecules. These processes lead to creation SEI layer. The SEI layer contains decomposition products from both solvents and Li atoms for example: Li_2CO_3, LiO_2, C_2H_4, CO_3^{2-} and other kinds of carbonaceous molecules which origin from electrolyte solvents. Among important SEI layer characteristics belongs ion conductivity (Li^+) and electron non-conductivity. At the further cell cycles is the SEI layer broadly stable. SEI layer formatting consumes Li atoms, if the Li atoms had not consumed on SEI layer, they would have contributed to battery capacity. The irreversible capacity mainly depends on electrode specific surface i.e. on electrode surface area that is in contact with electrolyte.

Is already good known that an irreversible capacity of graphite reduces total potential capacity of battery approximately from 15 % to 45 %. In our research we used two type of crystalline graphite – natural and expanded see Table I, these types are the most widely used material for negative electrode in Li-ion cells.
Our idea was to prepared a graphite mixture that should include intercalated Li atoms, these atoms could be used to creation SEI layer at first and second cycles and the whole potential capacity of Li-ion cells can be utilized.
The n-butyllithium (next n-BuLi) reagent that we used was dissolveat n-hexane with molar concentration 2.5 M.
We used mixture of solvents, ethylene carbonate (EC) and diethyl carbonate (DC) with lithium salt $LiPF_6$. [1]

2. Experiments

The first part of our work presents our study that deals with lithiation process with help of n-BuLi reagent. In this part we used the n-BuLi reagent this reagent should be according to our assumption reduce graphite material by its Li cations. Despite our hypothesis the n-BuLi reagent shown as too weak reagent that is not able to give its Li cations among graphite sheets. The total amount of intercalated Li atoms to graphite was very small almost negligible, see the results which are shown in paragraph A below. On the basis of these results was used iron(III) chloride, molecular formula $FeCl_3$. This ionic compound should be able to separate Li cations from butyl radical thus we might transfer lithium cations to graphite. This part of study is presented at part B of this paper.

A. Graphite lithiation with n-BuLi

First we prepared the materials for negative electrode, these materials were based on two types of graphite, see Table I below. Each specimen of graphite was dried for 12 hours at 150°C before its using in preparation process. This step is very important because the residual humidity in graphite might undesirable reaction with lithium that is contained at n-BuLi.

Table I. Properties of graphite materials.

GRAPHITE TYPE	PARTICLE DIAMETER [μm]	SPECIFIC SURFACE [$m^2.g^{-1}$]
Natural	< 11	10
Expanded	< 150	68

The manufacturing process is divided to several steps, which are listed below. All process operations were performed inside the glove-box under the inert argon atmosphere.

Manufacturing process steps

(1.) Drying of graphite specimens. This step is necessary because n-BuLi is very reactive with water and oxygen. We carried out this process in vacuum chamber at temperature 150°C for 12 hours.
(2.) Adding of n-BuLi. The BuLi is supplemented in ratio to graphite weight (one Li^+ ion on six atoms of carbon – LiC_6)
(3.) Stirring. The mixture make up from n-BuLi and graphite is stirred for 24 hours under room temperature.
(4.) First filtering. The mixture contains graphite, n-BuLi and n-hexane. In order to remove residues from mixture, the mixture is stirred at n-hexane for second time.
(5.) Stirring. The mixture make up in a previous step is stirred for 24 hours under room temperature at n-hexane.
(6.) Second filtering. The mixture is after filtering in final state, it should not contain any residues, called „pure“ material.

The process steps, which are listed above, are given to us lithiated graphite in form of powder. Based on this powder is prepared electrode material to it is added PVDF (Polyvinylidene fluoride). Electrode material was coated on copper foil, the thickness of a coated layer was approximately (400 – 600) μm. After coating process was electrode sintered for 12 hours at temperature 50°C and subsequently it was pressed by pressure 2 tons /cm^2.

The final electrode was measured on potentiostat /galvanostat device in half-cell connections, where the counter electrode was made from metal lithium.

At first was compared our two graphite types which we used in our experiments see Fig. 1.

The second graph on Fig. 2 shows the difference between lithiated and non-lithiated of expanded graphite materials. The specimen which was not lithiated (broken line) has about 20% higher capacity than lithiated specimen (solid line).

Graph shown on Fig. 3 presents the difference between charge-discharge characteristic for lithiated (solid line) and non-lithiated (broken line). In this case, like in previous case of expanded graphite, is the similar situation, where non-lithiated graphite has a higher capacity then lithiated.

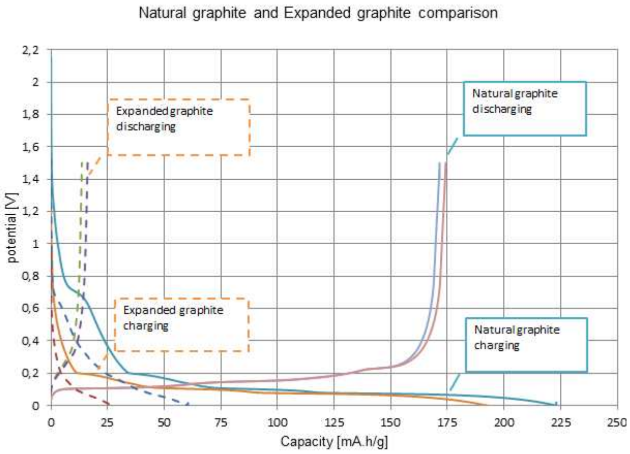

Fig. 1. Charge-discharge characteristics.

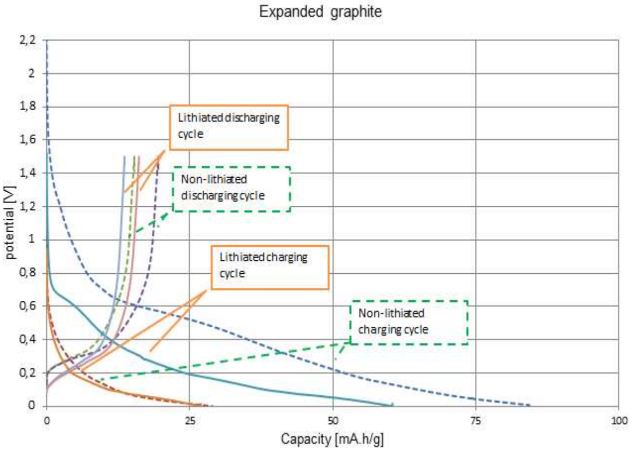

Fig. 2. Expanded graphite characteristics.

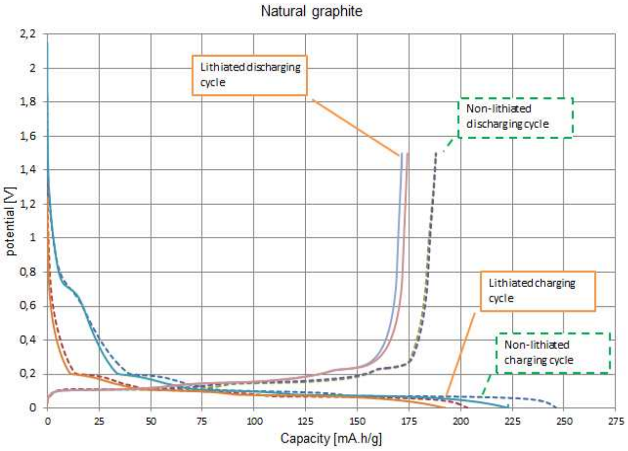

Fig. 3. Natural gaphite characteristics.

The lithiated graphite materials have got approximately similar irreversible capacity like non-lithiated. The non-lithiated natural graphite had the irreversible capacity around 24 % and lithiated natural graphite had 23 %, see Fig. 3. The bigger difference was observed in case of expanded graphite, Fig. 2 where non-lithiated specimen had the irreversible capacity around 82 % and in case of lithiated graphite has 77 %. The overall results, which show the total stable capacity and irreversible capacity, are shown in below.

Table II. Properties of lithiated grpahite materials

GRAPHITE TYPE	STABILIZED CAPACITY [mA.h/g]		IRREVERSIBLE CAPACITY [%]	
	LITHIATED	NON-LITHIATED	LITHIATED	NON-LITHIATED
Natural, CR 5995	188	203	23	24
Expanded	27	28	77	82

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

Second part of our study is based on results, which were measured in first part (*A. Graphite lithiation with n-BuLi*) and they are shown in Table II above. On this table is clearly seen that capacity of expanded graphite is very poor. The next all measurements were performed only with using natural graphite CR 5995. In terms of irreversible capacity we can see the slight difference between lithiated and non-lithiated graphite, from this point we assumed that Li atoms did not transfer from n-BuLi to graphite. For the other experiments we used chloride compound $FeCl_3$, this compound belongs to the group of ionic compounds named halides. Among halides we can include the compounds based on chloride that is combined with transition elements for example copper(II) chloride ($CuCl_2$), manganese(II) chloride ($MnCl_2$) and cobalt(II) chloride ($CoCl_2$). All the previously mentioned compounds are suitable for using in lithiation process, for our purposes seemed to be most appropriate using $FeCl_3$. [4]

Manufacturing process steps

(1.) Drying of graphite specimens as in previous step. Vacuum chamber at temperature 150°C for 12 hours.

(2.) Before using $FeCl_3$ we have dried it in vacuum chamber for 24 hours at 150°C. It is very important to remove the entire residual water from $FeCl_3$ powder.

(3.) After preparing graphite and $FeCl_3$ powder we prepared a mixture of both components. This process step was performed under inert atmosphere (Ar).
Were prepared two kinds of mixture, each mixture distinguished from the other in the ratio of $FeCl_3$ to C_6. The ratio was calculated on basis of hexagonal crystal structure of graphite sheets.
  - first one that contains one $FeCl_3$ per ten carbon atoms, ratio 10:1
  - second one that contains one $FeCl_3$ per six carbon atoms, ratio 6:1

The powder mixtures in exact ratio, was stirred with n-hexane for 24 hours for homogenization purpose.

(4.) The mixture contains graphite, $FeCl_3$ and n-hexane was filtered to remain n-hexane solvent from mixture. In this way we are able to prepare an exact mixture of graphite and $FeCl_3$.

(5.) At the last process step was added n-BuLi to the mixture, which was prepared in the point *(4.)* above.
The mixture with n-Buli was stirred for 24 hours and after this time it was again filtered. After this process we got the lithiated powder that is ready to create a negative electrode.

This way prepared electrode material was put on the copper foil, which represents electrode connector. To the electrode material as lithiated graphite powder was supplemented binder component. Like in previous electrode material was used PVDF binder that took 10 wt% of the entire electrode material. The prepared electrodes were measured in cell in that was connected to the galvanostat/potentiostat device and subsequently was performed charge–discharge measurement technique. The results of these experiments are shown on Fig.4 and 5.

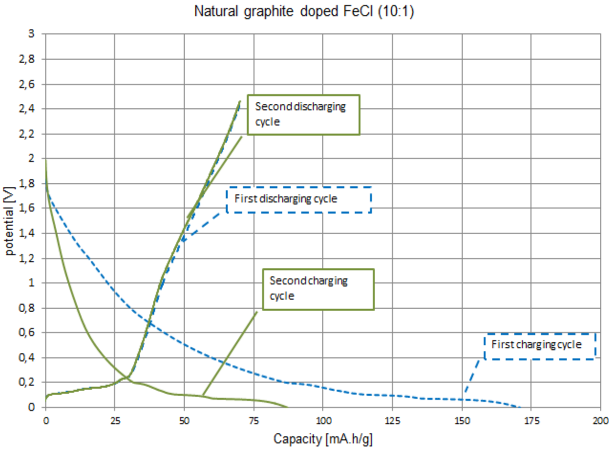

Fig. 4. Charge – discharge characteristics for graphite doped by FeCl3 in the ratio ratio 10:1.

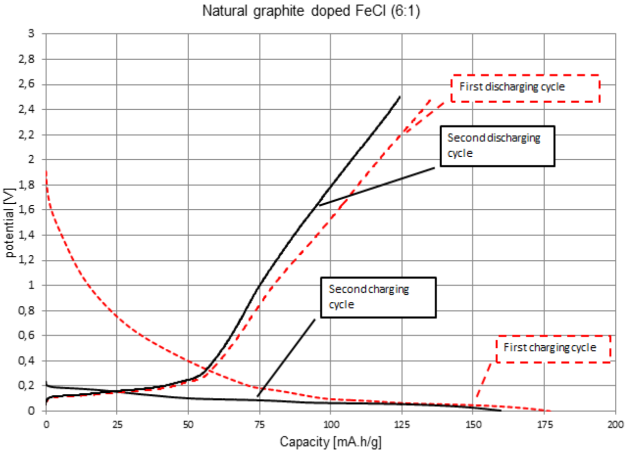

Fig. 5. Charge – discharge characteristics for graphite doped by $FeCl_3$ in the ratio ratio 6:1.

As you can see on figures above the stable capacity of specimen „10:1" is very low (around 85 mA.h/g) and also its irreversible capacity is much higher 58 % against the specimen that had the ratio „6:1", see Fig. 5. The specimen with the ratio „6:1" had the stable capacity around 160 mA.h/g and the smallest irreversible capacity 15 % from the all specimens. The capacity depends on the concentration (ratio) of $FeCl_3$ at an electrode material.

These differences are compared on Fig. 6 below, the closing results of this part of experiment are summarised in Table III.

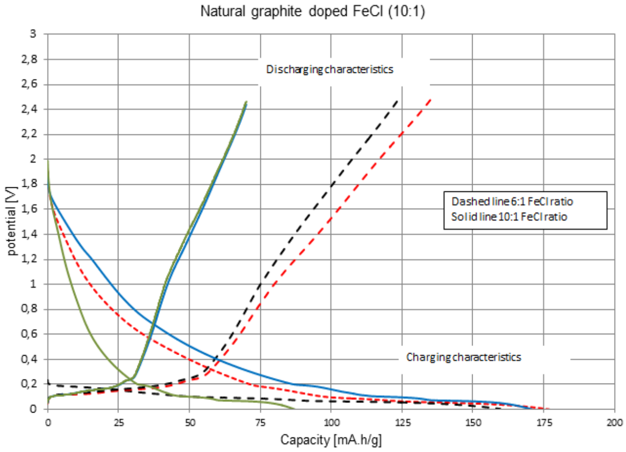

Fig. 6. Comparison of two $FeCl_3$ ratio.

Table IIII. Properties of lithiated grpahite materials wich were doped with $FeCl_3$.

RATIO NG CR5995: $FeCl_3$	STABILIZED CAPACITY [mA.h/g]	IRREVERSIBLE CAPACITY [%]
10:1	87	58
6:1	162	15

Note
The initialism NG means Natural Graphite.

Conclusion

In the first part of our study we describe the process in which we used n-BuLi with two kinds of graphite to preparing pre-lithiated graphite mixture.

In Fig. 2 and 3 are shown charge-discharge characteristics of both kinds of graphite. The expanded graphite could be caused by the bigger distances between sheets, bigger distance induces their decomposition by n-hexane, that penetrate among them. In the case of natural graphite, this behaviour is not observed because its smaller graphite sheet distances do not allow to penetration n-hexane, the measured date are listed in Table II. above. The small capacity and high irreversible capacity of expanded graphite caused the excluding of this kind of graphite out of the other experiments.

The n-BuLi reagent showed as too feeble reduction agent for graphite. The Li^+ cations do not able to intercalate in sufficient amount among graphite sheets. For enhancing the reducing potential of n-BuLi was supplemented graphite powder by iron(III) chloride ($FeCl_3$), ferric compound with ionic character.

The *B.* part of this paper is based on the results which we obtained in the part *A.* We used the ionic additive in powder form, in our case $FeCl_3$. This substance was added to the graphite with which it made a homogeneous mixture. This homogenous mixture was lithiated with help of n-BuLi reagent, like in the previous case in part *A.* of this paper. The measured results (from part *B.*) are present in Table III. above, the overall results (from both parts) are summarised and compared in Table IV. below. The table IV. includes only Natural graphite specimens, the expanded graphite has been shown as inappropriate for our purposes.

Table IV. Closing comparison of measured results.

KIND OF ELECTRODE MATERIAL (NG CR 5995)	STABILIZED CAPACITY [mA.h/g]	IRREVERSIBLE CAPACITY [%]
Pure NG CR5995	203	24
Lithiated NG CR 5995	188	23
Dopped $FeCl_3$ (10:1)	87	58
Dopped $FeCl_3$ (6:1)	**162**	**15**

Note

- *Pure NG CR5995, is origin graphite material based on Natural graphite without any modifications.*
- *Lithiated NG CR5995, is Natural graphite lithiated with 2,5 M n-BuLi.*

The results, which are listed in Table IV above, show the decreasing of irreversible capacity the Natural graphite specimen. The results also show that the lithiation process with help of n-BuLi can be successful and they proved that the idea related to decreasing of irreversible capacity using pre-lithiated graphite actually works.

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