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SHORT COMMUNICATION

Expanded graphite as an intercalation anode material for lithium systems

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Abstract The expanded graphite (BOCHEMIE a.s., Czech Republic) was tested as the material for anodes of lithium secondary batteries. The irreversible charge was lowered and the cyclability improved if the material was annealed in CO_2. The specific capacity approached theoretical value corresponding to the composition LiC_6.

Keywords Graphite · Anode · Mild oxidation CO_2

Introduction

Intercalation compounds are created from materials which posses layer structure. Among them, the first to be described were the compounds based on graphite [1] or on layered dichalcogenides, and the process of their formation was called intercalation. The process consists in penetrating of sufficiently mobile particles—guest—into the interlattice space (van der Waals layers) in the host. The theoretical concentration limit for intercalation of lithium into graphite is given by bonding of one atom of Li on a hexagonal structural unit of graphite, which is described by the formula LiC_6.

Metallic lithium is commonly used as an anode material in lithium primary batteries. Among its main advantages are the high specific energy and specific charge related to the mass unit and the longest lifetime of all primary batteries due to negligible self-discharge. Moreover, a voltage of 3 V or more can be achieved, which is quite sufficient in most microelectronic devices. On the other hand, lithium metal as a negative anode for secondary cells—rechargeable accumulators, did not prove successful and was soon replaced by other materials, safer and with a longer lifetime expressed by a number of charging–discharging cycles. In these batteries, both electrodes are basically of the intercalation type. When they are operating, lithium ions move from one electrode to another, while no morphological changes in electrodes materials occur. The concentration of salt in the electrolyte remains constant, and only a small amount of electrolyte is enough to keep the cell working. Batteries of this type have been called "rocking chair" or "shuttle cock."

In the production of these batteries, a phenomenon well-known as the irreversible capacity [2] is encountered. Organic electrolyte is decomposed by catalysis on the surface of graphite particles and an ion-conducting film originates. Charging efficiency in initial charging is thus substantially decreased.

In theory, the magnitude of the specific charge is usually considered by the limiting composition of a charged electrode corresponding to the intercalation compound given by the formula LiC_6.

In the Czech Republic, expanded (exfoliated) graphite is produced by the company BOCHEMIE a.s. Its particles are substantially enlarged through a chemical process, and a product called "expanded graphite" is manufactured and

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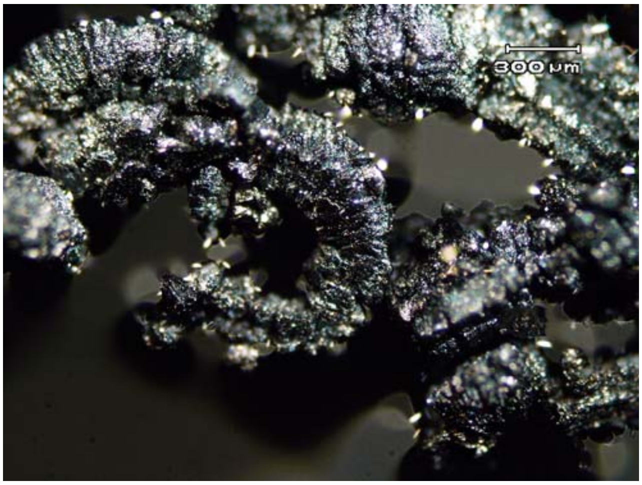

Fig. 1 The particles of expanded graphite

used as conductive component in materials for electrochemical power sources. Despite of the voluminous nature, the material is well conducting and has rather high possibility for electrochemical intercalation reactions. This research was initiated on the request of the manufacturer. A question arose if the material can be used as high-quality material for the production of negative electrodes in secondary lithium cells. The results of its investigation are given in this communication.

Materials and methods

Expanded graphite is produced by the company BOCHEMIE a.s., Czech Republic. For some experiments, it was modified by annealing for 1 h to 950 °C in CO_2 atmosphere analogically to [3, 4]. Then polyvinylidene difluoride (Aldrich, powder) was added in the amount corresponding to 5% and the material was pressed on a nickel screen. For comparison, powder graphite CR 5995 (Maziva s.r.o., Týn n. Vlt.) is used as a precursor for production of expanded graphite and its properties are described here for comparison.

Table 1 Morphological and surface properties of starting graphite CR 5995, exfoliated graphite EG-6, and exfoliated graphite EG-6 after the treatment in CO_2

Property	CR 9555	Expanded graphite as received	Expanded graphite annealed in CO_2
BET area ($m^2\ g^{-1}$)	4.6		6.3
BJH cumulative adsorption ($m^2\ g^{-1}$)	5.5	0.2275	5.94
BJH desorption ($m^2\ g^{-1}$)	8.7	0.003	7.63
Cumulative pore volume ($cm^3\ g^{-1}$)	0.0127	0.008	0.021
BJH pore radius (μm)	15.5	165.8	19.09

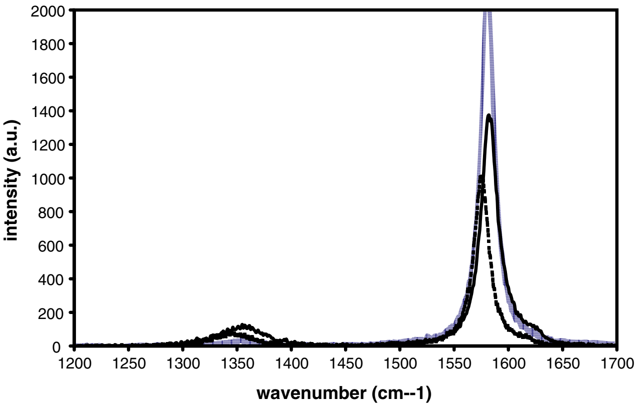

Fig. 2 Raman spectrums of raw graphite CR 5995 (*dotted line*), expanded graphite as received (*solid line*), and expanded graphite annealed in CO_2 (*gray line*)

No impurities were detected in the final material using the EDAX analyzer in a SEM microscope. The morphological properties were measured by means of a device from Quantachrome Instruments.

Electrodes were prepared by pressing the material onto a nickel screen (approximately 1 cm^2 of apparent surface area) and inserted into conventional three-electrode vessel containing lithium counter and reference electrodes. No pressure was applied during the experiments.

Electrochemical measurements

The 1 M solution of anhydrous $LiClO_4$ was prepared from dry mixture of ethylene carbonate–diethyl carbonate (EC–DEC) in the ratio 1:1. A three-electrode cell containing metal lithium as an auxiliary and reference electrodes was used for measurement.

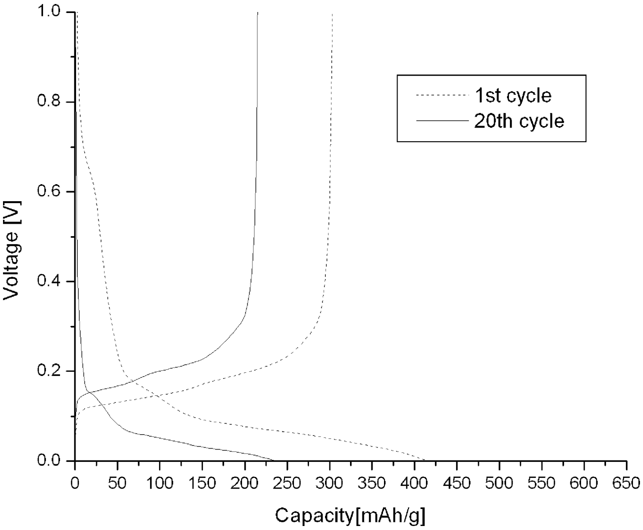

Fig. 3 Galvanostatic charging–discharging curves of graphite CR 5995 cycles no. 1 and 20

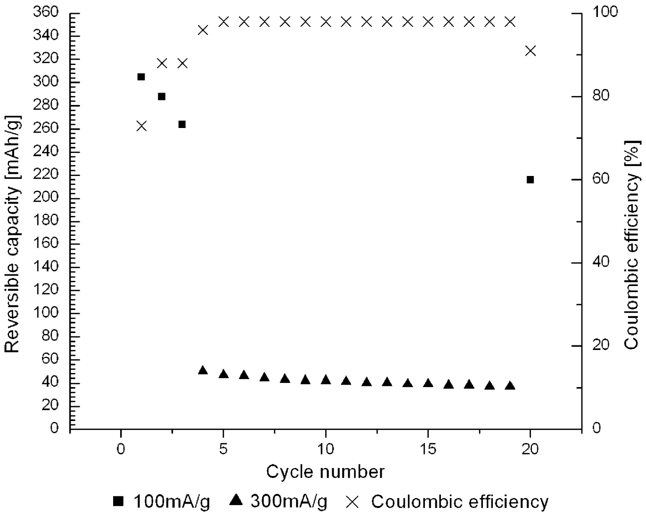

Fig. 4 Summarized properties of graphite CR 5995. *Crosses* Coulombic efficiency, *squares* current 100 mA/g, *triangles* current 300 mA/g

Galvanostatic measurements were executed with current corresponding to 100 or 300 mA/g of active substance between potentials and 1.5 V (vs. Li) in such a way that the first cycle started in the direction of charging the negative electrode (cathodically).

Results and discussion

Thanks to their shape, the particles of expanded (or exfoliated) graphite are sometimes called “worms” or “shrimps,” as it is demonstrated in Fig. 1. Morphological and surface properties of starting graphite CR 5995, exfoliated graphite EG-6, and the same after the treatment in CO_2 are given in Table 1.

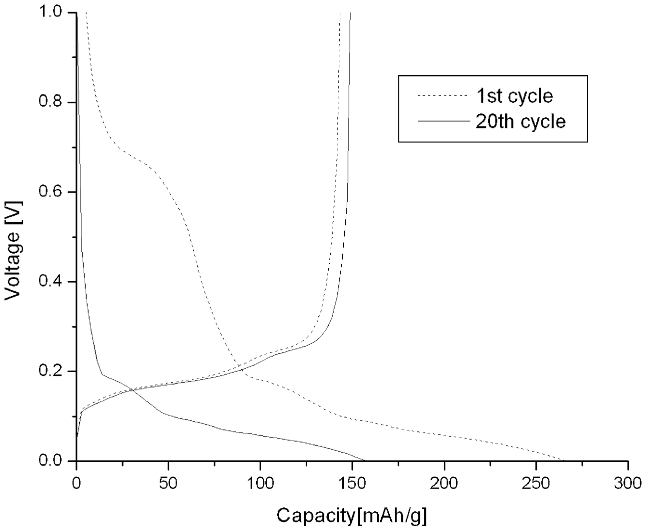

Fig. 5 Galvanostatic charging–discharging curves of expanded graphite cycles no. 1 and 20

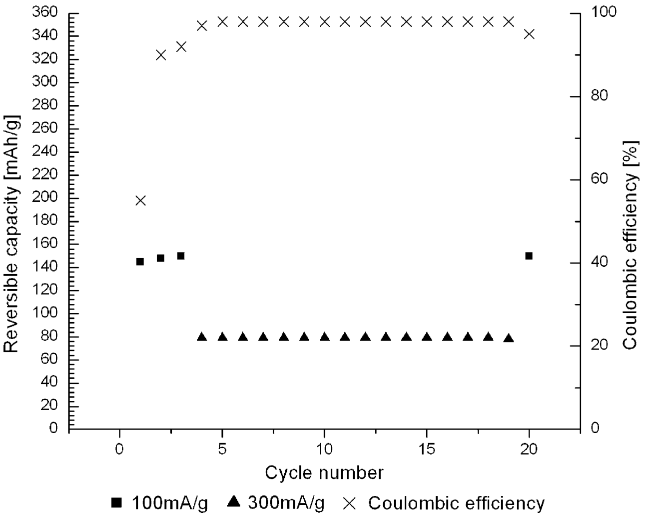

Fig. 6 Summarized properties of expanded graphite. *Crosses* Coulombic efficiency, *squares* current 100 mA/g, *triangles* current 300 mA/g

The starting materials were investigated briefly by Raman spectroscopy. The Raman spectrums are shown in Fig. 2. All materials under investigation exhibited two lines. The stronger of them at wave number 1,565–1,575 cm^{-1} with a small trace of asymmetry or a side shoulder is ascribed usually to band G and it is caused by sp^2 bonded carbon atoms in graphene layers. The other line at 1,350–1,360 cm^{-1} corresponds to dangling bonds and other defects in-plane in graphene layers and is considerably weaker than the former one [5].

Results are given in Figs 3, 4, 5, 6, 7, and 8 in such a way that, for each material, cycle 1 and 20 are compared. The next figure shows the development of reversible capacity and charging efficiency during all cycles. The results are summarized in Table 2.

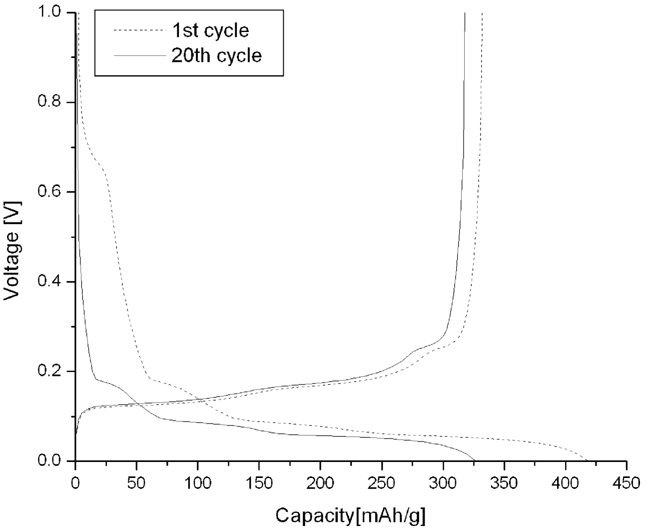

Fig. 7 Galvanostatic charging–discharging curves of expanded graphite annealed in CO_2

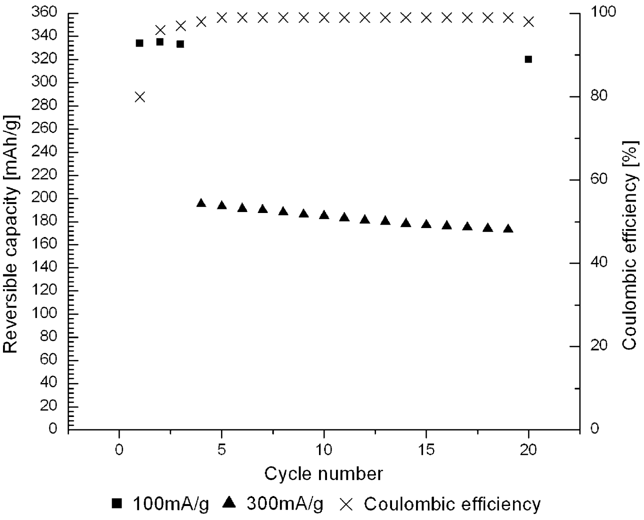

Fig. 8 Summarized properties of expanded graphite annealed in CO_2. *Crosses* Coulombic efficiency, *squares* current 100 mA/g, *triangles* current 300 mA/g

The results lead to the following description:

1. Charging efficiency is low for the original graphite and it is the highest for graphite treated by annealing in CO_2 and approaches to the theoretical value for intercalation compounds with staging equal to 1.
2. The irreversible charge of the first cycle is the lowest in the sample treated by annealing in CO_2. On the contrary, in expanded graphite without annealing, the irreversible charge is markedly higher than in expanded graphite with annealing.
3. Both samples of expanded graphite display a substantially lower capacity decrease while the current density goes up from 100 to 300 mA/g, which indicates a better electric contact between these material particles.
4. The lifetime of the material is improved by annealing in CO_2.
5. From comparison of porosity and Raman measurements, a conclusion can be drawn that the increase of internal pore volume is responsible for the improvement of material quality.
6. The ratio of both Raman signals gives some weak evidence that the annealing in CO_2 *decreases* the number of dangling bonds and defects. The decrease of irreversible charge in the first charging cycles could be explained in this way.
7. The annealed graphite offers higher current load than the untreated one.

Discussion

The process of graphite expansion changes their morphology in such way than they are called “worms” or “shrimps,” as shown on Fig. 1. Their strongly disintegrated shape enables neighboring particles to remain in good contact, which facilitates the transfer of current between them.

The treating in CO_2, which was used several times for the activation of various kinds of carbon for the use in double layer supercapacitors, undoubtedly increases the porosity of the material even if overall surface area is not changed too much (see Table 1).

Cleavage of individual graphene layers could change the shape of the particles. In such a situation, we could hardly see any intercalation between them. However, the material—despite the creation of micropores and nanopores—still remains coherent. A comparison offers of the process similar to the explanation given by Huggins [6] and coworkers on the example of lithium insertion into nanofibers of silicon. They have declared that the nanostructure can accept extreme increase of particle volume by insertion as well as its shrinking almost to original size by lithium extraction. In the case of Li–Si system, the change of volume is larger than 400%, and the weakly bonded nanostructure can compensate the volumetric changes. We expected something similar in the case of expanded graphite thanks to great voluminosity of its particles.

However, the weaker formation of surface film and decrease of “irreversible capacity” in the first charging cycle cannot be justified by morphological changes only. It is quite probable that CO_2 reacts with surface groups such as ketonic groups or—generally speaking—compounds containing C–O bonds. Also, the saturation of “dangling bonds” discussed frequently in the description of semicon-

Table 2 The development of reversible capacity and charging efficiency during all cycles

Graphite	CR 5995	EG	EG CO_2
Reversible capacity 1st cycle (100 mA/g)	305	145	334
Irreversible capacity 1st cycle (mA/g)	111	121	83
Irreversible capacity 1st cycle due to SEI formation (mA/g)	25	52	27
Coulombic efficiency 1st cycle (%)	73	55	80
Coulombic efficiency 10th cycle (%)	98	98	99
Reversible capacity 4th cycle (300 mA/g)	50	79	195
Reversible capacity 20th cycle (mA/g)	216	150	320

ductor surface might be satisfied by some reaction with CO_2.

As the main problem connected to this material is very low volumetric density (apparent density is in the range 0.2 to 0.3 g cm^{-3}), which needs to be solved for technological applications, more extended investigations, e.g., by Raman spectroscopy, are in the course of preparation.

Conclusions

The expanded graphite (BOCHEMIE a.s., Czech Republic) was tested as the material for anodes of lithium secondary batteries. The irreversible charge was lowered and the cyclability improved if the material was annealed in CO_2. The specific capacity approached theoretical value corresponding to the composition LiC_6.

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References

1. Pistoia G (ed) (1994) Lithium batteries, chapters 1 and 2, industrial chemistry library, vol. 5. Amsterdam, Elsevier
2. Winter M (2007) The electrolyte in lithium batteries. In: Lithium mobile power. The Knowledge Press, Brookline, USA, p 183
3. Menachem C, Wang Y, Flowers J, Peled E, Greenbaum SG (1998) Characterization of lithiated natural graphite before and after mild oxidation. J Power Sources 76:180–185 doi:10.1016/S0378-7753(98)00167-0
4. Wu YP, Jiang C, Wan C, Holze R (2003) Anode materials for lithium ion batteries by oxidative treatment of common natural graphite. Solid State Ion 156:283–290 doi:10.1016/S0167-2738(02)00680-X
5. Li L, Zhu ZH, Yan ZF, Lu GQ, Rintoul L (2007) Catalytic ammonia decomposition over Ru/carbon catalysts: the importance of the structure of carbon support. Appl Catal A Gen 320:166 doi:10.1016/j.apcata.2007.01.029
6. Chan CK, Peng HLm, Kiu G, Mc Ilworth K, Zhang XF, Huggins RA, Cui Y (2008) Nat Nanotechnol 3:31