

Synthesis and characterization of graphite/silicon composites for energy storage in lithium batteries

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Introduction

Rechargeable lithium batteries (Li-ion batteries) are widely regarded as the most advanced family of electrochemical energy storage devices. Since the first commercialization in 1991 by Sony Corp. this type of batteries has achieved a tremendous success in terms of technological development and number of covered applications. Besides being today a conventional power source for virtually all kinds of portable electronic equipment like computers, cell-phones, cameras, etc., Li-ion batteries, they are also widely considered as electricity sources for such demanding future applications as electric vehicles, medical and military equipment or instruments for aerospace exploration.

Intensive research efforts are still devoted to increase the reversible capacity of anodic materials for Li-ion batteries. Reversible capacity is directly connected to the duration of a device operation on single battery charging, thus, is of vital importance for the user of electronic equipment. Carbons, in particular graphite-based materials, are widely recognized as the most attractive candidates for technologically viable anode materials. The most obvious drawback of graphite, however, is its charge capacity inherently limited to 372 mAh/g, which is related to the number of lithium cations that can be located in the crystal lattice of graphite (one lithium atom per six carbon atoms for fully lithiated Li-graphite intercalation compound at ambient pressure). In order to increase energy densities of the next generations of Li-ion batteries, it is necessary to search for anode materials allowing for much more charge to be stored per mass unit of electrode active materials. In recent years a lot of research works have been focused on combining two elements, namely – silicon and carbon – as prospective composite anodic materials [1 ÷ 10]. It is well known that pure silicon has an extremely high ability for lithium storage ($\text{Li}_{4.2}\text{Si}$ alloy compound gives a theoretical capacity of 4200 mAh/g, as compared to 372 mAh/g for ideal graphitic materials), however, without a good capacity retention during prolonged cycling. Unfortunately, the gradual capacity loss is observed during the first few cycles due to serious volumetric changes upon lithium cation insertion/deinsertion. This causes great stress in Si lattice and thus leads to cracking and mechanical disintegration of the electrode. As a result, some of the particles may lose electrical contact leading to the observed capacity loss.

Our objective was to investigate the effect of combining graphite and silicon in the process of high energy ball milling on charge/discharge capacity and its retention during cycling. The motivation of our work was to check if encapsulation of silicon particles in mechanically disordered graphite matrix may help in accommodating volume changes associated with lithium insertion into silicon. Normally carbon anodes are charged down to the potential of 0 V vs. Li/Li^+ . Taking into account that lithium insertion/deinsertion in Si crystal lattice occurs at more positive potentials, the effect of modifying the charging cut-off voltage has also been examined.

Experimental

Graphite SL-20 (Superior Graphite) with particle size from 20 to 40 μm and low specific surface area ($< 5.5 \text{ m}^2/\text{g}$) has been used

for all the experiments. The material is specially purified to obtain rounded flakes, particularly suitable for Li-ion batteries. Silicon particles (Aldrich, 45 μm average particle diameter, 99% purity) were used for preparing C/Si composites (Si content from 5 to 50%). The high-energy ball milling was applied for 10 hours with the application of Retsch MM200 mixer using zirconium balls. Scanning electron microscopy (Vega@Tescan apparatus) and X-ray diffraction measurements have been undertaken for physical characterization of the obtained composite samples. Electrochemical studies have been used to estimate the Si/C composite lithium storage ability upon cycling. MacPile potentiostat/galvanostat (BIOLOGIC, France) has been used for electrochemical tests (cyclic voltammetry at 0.05 mV/s scan rate and galvanostatic charge/discharge). Materials were tested in two-electrode Swagelok-type electrochemical cells with metallic lithium counter/reference electrodes. Working electrodes have been prepared by casting a viscous slurry containing the examined composite material, polymeric binder (5% by weight) and the solvent (N-methylpyrrolidone) onto a copper current collectors, followed by drying under vacuum at 120°C for at least 12 h. All operations are carried out in argon filled glove box (humidity level below 1 ppm). As an electrolyte in the electrochemical studies was used LiPF_6 (1 M, Aldrich, 99.99%) in a 1:1 mixture of ethylene carbonate (anhydrous, 99%, Sigma-Aldrich) and dimethyl carbonate (anhydrous, 99%, Sigma-Aldrich).

Results and discussion

The process of high energy milling in shock-type ball mill not only pulverizes the sample and homogenizes two components of the composite, but also introduces structural disorder to materials. It is clearly evidenced by comparing XRD patterns of graphite before and after milling (Fig. 1).

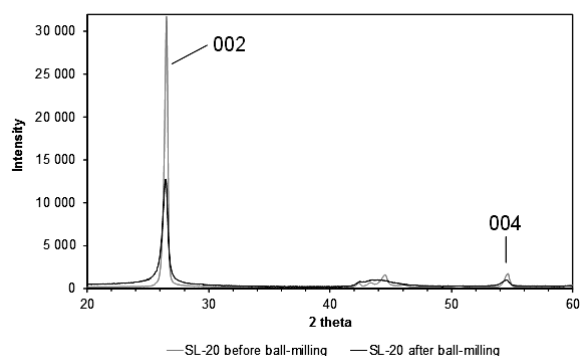


Fig. 1. Effect of milling on the XRD pattern of SL-20 graphite

Significant broadening of 002 (FWHM = 0.32 deg) and 004 (FWHM = 0.48 deg, where FWHF – full width at half maximum of the diffraction peak) peaks is a good indicator of crystallite size diminishing along the crystallographic axis c. Also scattering angle region between ca. 41 and 48 degrees 2θ exhibits features of vanishing three-dimensional order in the graphite lattice.

Figure 2 shows SEM image in BSE mode for the ball-milled composite with 50% Si. It seems that Si component is fairly and homogeneously admixed with graphite. Because of the different atomic masses of both elements Si domains can be observed as light spots on dark background. It is rather arbitrarily accepted in the present work that Si distributed in graphite matrix, not otherwise. The right picture in the Fig. 2 shows XRD patterns recorded for the ball-milled composites with various Si contents, starting from pure graphite SL-20. Obviously, the silicon diffraction peaks increase their intensities as Si content rises. It is noteworthy, however, that during prolonged milling carbide SiC is not formed (no SiC peaks are observed), although such a process might be expected as a result of interfacial solid state reaction with interphase atomic diffusion between graphite and Si. This fact is advantageous since silicon carbide is known to be electrochemically inactive in terms of lithium insertion.

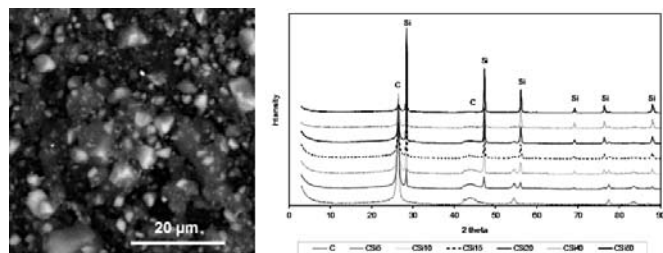


Fig. 2. Distribution of silicon in C/Si composite with 50% Si (left picture) and XRD patterns recorded for the ball-milled composites with various Si contents

The milling process causes significant fragmentation and destruction of the structure of the graphite flakes. Figure 3 presents SEM images of some of the investigated ball-milled composites in comparison to individual components. Rounded shape of original SL-20 graphite particles is visible in Figure 3a. On the other hand, a strong degradation is shown after shock mode milling (Fig. 3b). Original Si particles are presented in Figure 3c whereas the milled graphite/Si composites with different Si contents (5%, 20% and 50% of Si) are shown in Figures 3d, 3e and 3f, respectively. SEM observations clearly illustrate that silicon particles are homogeneously embedded in the matrix of crushed graphite flakes.

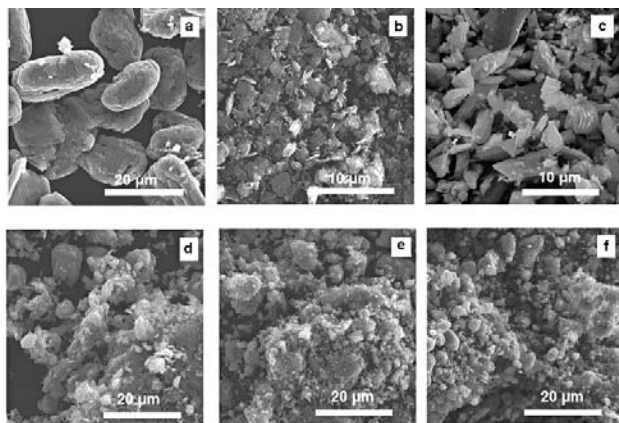


Fig. 3. SEM micrographs for different samples: a) original graphite SL-20; b) ball-milled graphite SL-20; c) original silicon; d) ball-milled composite with 5% Si; e) ball-milled composite with 20% Si; f) ball-milled composite with 50% Si

Composites with different amounts of silicon have been investigated electrochemically in two electrode cells composed of lithium (counter/reference electrode) and C/Si composites as working electrodes, in order to evaluate their lithium storage capacity. Preliminary experiments (three cycles) by voltammetry technique at 0.05 mV/s scan rate have been performed to identify the best material composition. Figure 4 shows cyclic voltammograms

for milled graphite (Fig. 4a) and three selected composites (Figs. 4b, 4c and 4d). Voltammogram recorded for pure graphite exhibits typical features of this kind of lithium insertion material. Large irreversible peak with maximum at ca. 550 mV vs. Li/Li⁺ can be seen on the cathodic side in the first cycle, practically disappearing in the subsequent cycles. This peak is obviously associated with the formation of solid electrolyte interphase (SEI) on graphite as a result of the decomposition of electrolyte components. Addition of silicon to the electrode mass results in the appearance of new current signals, particularly well developed on the oxidation (lithium deinsertion) sides of the curves. Large portion of electrical charge is now discharged at significantly higher potentials. It is evident in the case of 50% of Si, where most of charge is being removed in the potential region around 0.5 V vs. Li/Li⁺. In practical terms this will implicate that voltage of the Li-ion battery will be lower as compared to batteries with purely graphitic anodes. Taking into account a significantly higher storage capacity, the sample with 20% of Si has been selected for more detailed electrochemical study.

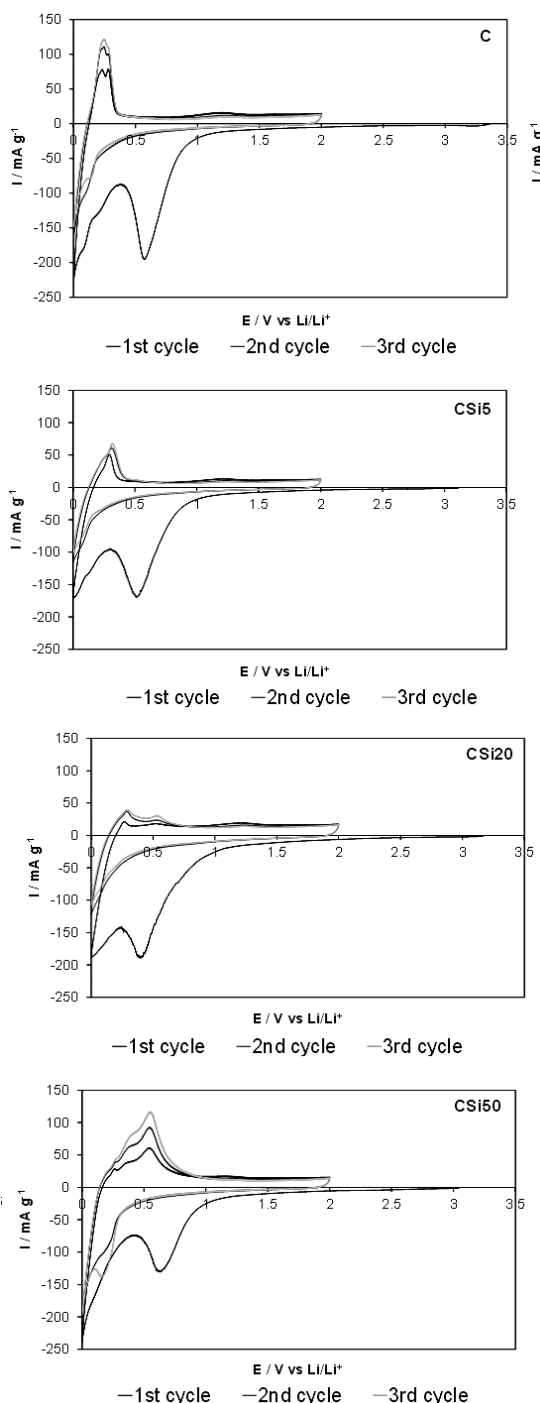


Fig. 4. Voltammetry characteristics (0.05 mV/s scan rate; scanning between 0 and 2 V vs. Li/Li⁺) for samples with a different content of silicon: 0% Si, 5% Si, 20% Si, 50% Si

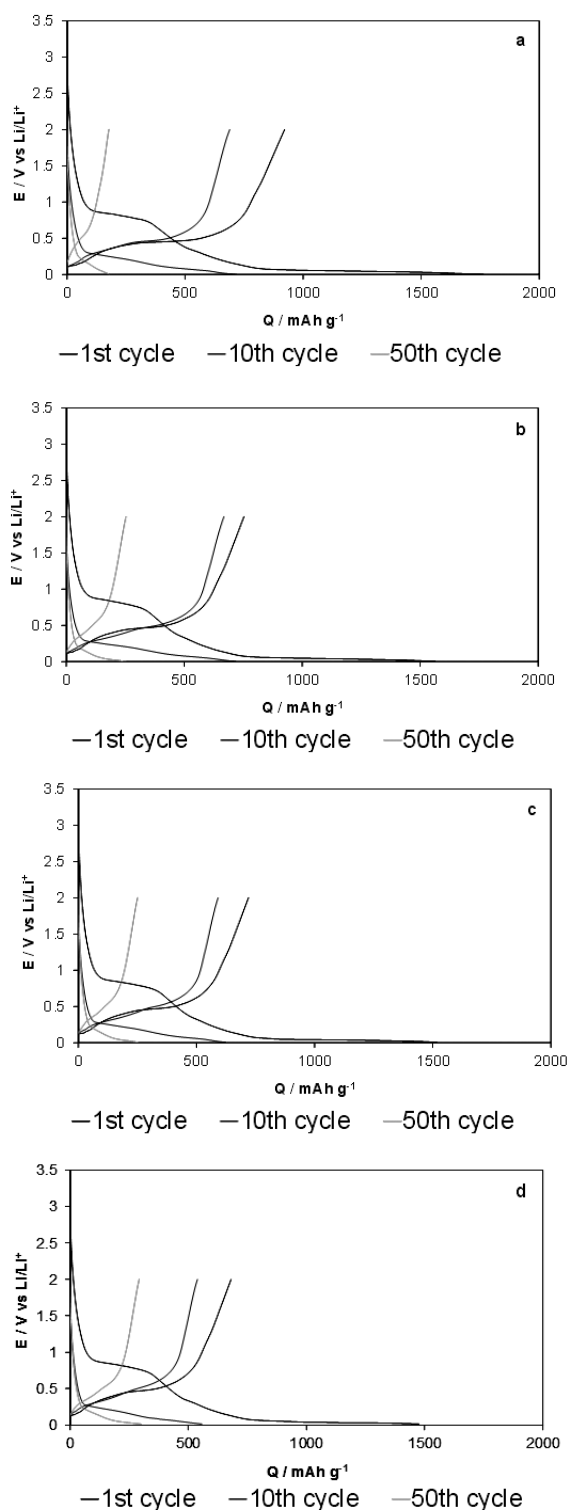


Fig. 5. Galvanostatic charge/discharge characteristics for the ball-milled C/Si composite with 20% Si at different end-of-charge potentials (vs. Li/Li⁺) a) to 0 V; b) to 5 mV; c) to 10 mV; d) to 15mV

Figure 5 presents constant current charge/discharge characteristics for the C/Si composite anode with 20% Si. Earlier reports and conventional knowledge suggest that in the case of graphite/Si composite metallic Li deposition may appear during charge to 0 V vs. Li/Li⁺ due to lithium insertion overpotential, which might contribute to the shortening of cycle life. Hence, our study was additionally designed in such a way that lithium insertion (charging) was stopped at different potentials higher than conventional 0 V. End-of-charge potentials (EOCP): 0mV, 5mV, 10mV and 15mV (vs Li/Li⁺) have been applied. The effect is reflected in the observed discharge capacities (see Fig. 5 as well as Tab. I for numerical data). When comparing discharge capacities in the first cycles only, one can observe that the examined C/Si composite exhibits huge reversible

capacities (Q_{dis} up to 921 mAhg⁻¹ at 0 V EOCP) and elevating the EOCP results in consistent diminishing Q_{dis} (down to 682 mAhg⁻¹ at 15 mV EOCP potential. Although 15 mV vs. Li/Li⁺ may seem to be negligible, large portion of charge is in fact lost by such a cut in EOCP due to the fact that very important fraction of lithium cations is located in the crystal structure of silicon at potentials extremely close to 0V. However, when comparing discharge capacities in the 50th cycles, the capacities clearly tend to rise together with increasing the EOCP (177mAhg⁻¹ at 0V vs. Li/Li⁺ EOCP versus 293mAhg⁻¹ at 15mV vs. Li/Li⁺ EOCP). Although there is still a big capacity drop upon cycling, the study demonstrates that EOCP is an important factor by which this unwanted phenomenon can be alleviated to some extent.

Table I

Values of charge/discharge capacities during cycling for graphite/Si composite with 20% of Si end-of-charge potentials

End-of-charge (EOC) potential (vs. Li/Li ⁺)	Cycle number	Q_{ch} / mAhg ⁻¹	Q_{dis} / mAhg ⁻¹	Q_{irrev} / mAhg ⁻¹
0 mV	1	1765	921	844
	10	719	689	30
	50	181	177	4
5 mV	1	1563	753	810
	10	719	668	51
	50	260	253	7
10 mV	1	1517	720	797
	10	623	592	31
	50	256	251	5
15 mV	1	1476	682	794
	10	558	539	19
	50	301	293	8

Another possible explanation of the reversible capacity increase during prolonged cycling is that both composite components become gradually more and more compatible. Together with repeated volume changes of silicon, the Si domains dispersed in the flexible carbon matrix created by ball milling start to fit more and more closely, thus gaining better electrical contact.

Conclusion

Graphite/silicon composites have been prepared by a high energy ball milling in shock mode, characterized structurally and examined in terms of electrochemical lithium insertion/deinsertion. The milling process homogenizes components of the composite materials, nevertheless, the impact of silicon components on the electrochemical performance is very strong and rising with increasing Si content. The composition with 20% of Si seems to have the best electrochemical properties among the tested, considering the mutually opposing factors of reversible and irreversible capacities.

Electrochemical behavior appear to be very sensitive to the end-of-charge potential (EOCP) applied to the cells upon galvanostatic cycling. When EOCP is shifted by only 15 mV vs. Li/Li⁺ towards positive values, the recorded reversible capacities drop in the first cycle, but rise upon prolonged cycling. This important finding may be attributed to the avoidance of metallic lithium stripping on the anode as well as to the mutual accommodation of both composite components in each other. Although in our work the capacity retention is still not satisfactory, the combination of ball milling of silicon with graphite and tailoring the anode end-of-charge potential may be regarded as a promising direction for further, more in-depth, explorations.

Acknowledgements

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Translation into English by the Author

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Z prasy światowej – innowacje: odkrycia, produkty i technologie

From the world press – innovation: discoveries, products and technologies

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Inteligentne materiały kompozytowe

Zautomatyzowana produkcja lekkich i inteligentnych materiałów kompozytowych jest jedną z kluczowych technologii w przemyśle motoryzacyjnym. Nowoczesne koncepcje proponują wprowadzenie elementów inteligentnych poprzez umieszczenie w takim materiale zintegrowanych sieci sensorów. Sieci te są w stanie rejestrować najrozmaitsze sygnały fizyczne; mogą również działać jako elementy aktywne. Zazwyczaj inteligentne materiały kompozytowe wykorzystywane są do stałego monitorowania stanu strukturalnego. Na łamach czasopisma *Sensors and Actuators A: Physical* niemieccy naukowcy prezentują nową wysokonakładową technologię produkcji inteligentnych kompozytów, w których czujniki piezoceramiczne i elementy napędu umieszczono w kompozytach składających się z włókna szklanego impregnowanego poliuretanem. Technologia ta umożliwi przeprowadzenie procesów produkcji czujnika i wytwarzania inteligentnego elementu w jednym etapie. Doświadczenia potwierdziły skuteczność tak otrzymanych czujników piezoceramicznych. Eksperymenty wykazały również, iż opisywana technologia umożliwia integrację różnych elementów elektronicznych i baterii w strukturę materiałów kompozytowych. Łagodne warunki procesu, tj. niskie ciśnienie i temperatura, nie wpływają bowiem destrukcyjnie na delikatne elementy elektroniczne. (kk)

(A. Weder, S. Geller, A. Heinig, T. Tyczynski, W. Hufenbach, W.-J. Fischer: *A novel technology for the high-volume production of intelligent compositestructures with integrated piezoceramic sensors and electronic components*, *Sensors and Actuators A 202 (2013) 106–110*)

Sztuka wzmacniania, czyli 10 terawatów na biurku

Fizycy z Centrum Laserowego Instytutu Chemii Fizycznej PAN i Wydziału Fizyki Uniwersytetu Warszawskiego skonstruowali kompaktowy wzmacniacz optyczny nowej generacji. Przyrząd charakteryzuje się bardzo wysoką wydajnością, dzięki której aparatura laserowa mieszcząca się na biurku jest w stanie generować impulsy świetlne o mocy ponad 10 terawatów. Czy urządzenie zajmujące ledwie pół biurka może wytworzyć moc kilkadziesiąt razy większą od generowanej przez wszystkie elektrownie jądrowe świata? Odpowiedź brzmi: „w impulsie – tak”! Dzięki nowemu wzmacniaczowi parametrycznemu, na zwykłym stole optycznym udało się wyprodukować bardzo krótkie (femtosekundowe) impulsy laserowe o gigantycznej mocy 10 terawatów. Nowy wzmacniacz jest ważnym krokiem do budowy kompaktowych, przenośnych i relatywnie tanich urządzeń laserowych wielkiej mocy, które mogą zrewolucjonizować m.in. terapie antynowotworowe. (kk)

(<http://ichf.edu.pl>, 3.10.2013)

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