Short communication

Silicon/graphite composites as an anode material for lithium ion batteries

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Abstract

Mixed silicon–graphite composites have been prepared by means of mechanical milling process. Their micro-heterogeneous structure is considered responsible for electrode failures. A fingerprint of this process is seen by cycling the carbonaceous component of the composite in an electrolyte containing small amount of propylene–carbonate (PC). Local voltage drops close to 0 V (versus Li metal) resulted in local electrode mechanical deterioration. In the presence of silicon particles such local disorders would lead to a loose interparticle contact (zones called dead spots). Deterioration pattern of the mixed composite electrode may be considered as a set of 'dead spots' spreading across the electrode as the cycling proceeds. Hence, a careful optimization is necessary in order to fabricate composite electrode giving minimum local disorders and having satisfactory cycling performance.
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1. Introduction

Recently, there has been a worldwide interest in developing alternative anodes for lithium ion batteries. Fundamental reason for these studies relies on the fact that the potential of the anode versus Li is typically within 0.05–0.5 V, which means that the electrochemical reaction at the anode site should not necessarily be based on an intercalation type of reaction. Li-metal alloys are the natural alternative to the currently adopted intercalation hosts, such as $LiTi_2O_4/Li_4Ti_5O_{12}$, and different blends of natural or artificial graphite. An obvious advantage of the binary alloys is that the Li:M mole ratio in the Li_xM alloy at the end of charging can be much higher than in the case of intercalation hosts, since the latter generally cannot accommodate and release large amounts of Li^+ in order to maintain a stable crystal structure over the cycles. Actually, Li-metal alloys have been considered possible anodes even sooner than the currently adopted intercalation carbonaceous hosts. The first use of lithium alloy anodes was the employment of Wood's metal (alloy of Bi, Pb, Sn, Cd) in button-type cells developed by Matsushita-Panasonic [1–6].

The main drawback of these metal electrodes was that reasonable cycling life could be reached only for a very "shallow" cycling mode (<10% depth of discharge). As a result, the specific charge density of the first commercial alloying electrode was an order of magnitude lower than that expected for lithium rich alloys observed at high temperature. Deep cycling of lithium metal-free cells became possible when Sony introduced its carbon anode-based lithium ion cell in the beginning of 1990s [7,8]. First lithium-ion batteries employed hard carbon with practical capacity in the order of 200 mAh g^{-1}. Following the invention of new electrolyte additives, practical use of highly crystalline graphite has become possible. Modern graphite anodes have practical capacity in the order of 360 mAh g^{-1}, which is close to the theoretical stoichiometry with maximal Li uptake (LiC_6). Thus, the possibility of improving of carbonaceous anodes is almost exhausted. On the other hand, it is unlikely that significant improvement of the cathode materials can be realized in the near future. Therefore, the only possibility for further significant improving of the Lithium ion (LION) technology is to develop alternative anodes with a capacity several times higher than that of graphite. Such anodes can be developed by means of light metals from the groups III, IV and V of the periodic table, particularly Sn or Si. The latter two elements offer not only high theoretical capacity in an appropriate potential window, but

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are also abundant and environmentally friendly. Silicon-based anodes are more attractive, because Si is 4.2 lighter than Sn (atomic weights: Si 28.086, Sn 118.690) and their alloys with maximum lithium uptake (at elevated temperatures) have the same stoichiometry: $Li_{22}M_5$. Therefore, composite materials containing the same amount of Si instead of Sn would have a factor of 4.2 higher overall capacity for the same final Li_xM alloy stoichiometry.

2. Experimental

The active material used in this study was a mixture of *p*-Si (average particle grain size 1 μm supplied by Mitsui Kozan Co., Japan) and two types of carbonaceous materials: synthetic graphite (MCMB 6-28, Osaka Gas Co., Japan) and hard carbon (company name T4B2, SNC Co., Japan). The ingredients were premixed in a ball-mill (Fritsch, Germany) for 5 h at $250 \, min^{-1}$ under Ar. Balls to composite ratio was set to approximately 10:1 by weight. This active material was bound onto a copper foil current collector by means of a styrene–butadiene copolymer binder (SBR, trade name BM-400B, ZEON Co., Japan). Sodium carboxy methyl cellulose (CMC, trade name HB-45, ZEON Co., Japan) was used as a thickening/setting agent. This binder possesses stronger binding force, higher flexibility and heat resistance than the widely adopted polyvinylidene fluoride (PVDF). It is also water-soluble and therefore is not influenced by the atmospheric humidity. The composite electrode was prepared by means of the common method adopted by LIB industries. Dry Si/graphite composite was mixed with an appropriate amount of 1.73 wt.% CMC water solution and agitated in a bubble-free kneader (model NBK-1, NISSEI, Japan) for 6 min at $120 \, min^{-1}$. Then, an appropriate amount of 40 wt.% water suspension of SBR such that the dry electrode film contained 84 wt.% active material, 5 wt.% CMC and 11 wt.% SBR. The slurry was further agitated for 3 min, pasted on a copper foil or nickel foam current collector, and dried for 1 min in a stream of fresh hot air at approximately 100 °C. Circle-shaped electrodes were punched from the copper foil and tested in a coin cell versus Li metal. For the case of nickel foam current collector, a circle-shaped piece was cut from the nickel foam sheet. Its mass was measured prior to and after pasting the slurry, and the amount of the active material found by substracting both values bearing in mind the amount of the binder present in the composite electrode. Electrolyte used in this study was 1 M $LiPF_6$ dissolved in EC/DMC (3:7) kindly supplied by UBE Chemicals, Japan.

3. Results and discussion

It is well-known that despite their appropriate features, binary Li–M alloys are yet to be commercialized as practical anodes for LIB, because of the large volumetric variations of the parent metal phase reacting with Li^+. It leads to a morphological instability of the electrode, followed by a loose electronic contact with the current collector and electrode disintegration, which is considered the reason for the poor cycling behavior of composite metal-containing electrodes. As shown in [9] there should be limiting particle size under which the particles do not crack despite of the large volumetric variations. Our previous studies showed that this particle grain size is approximately 1 μm and composites containing silicon particles with such or smaller grain sizes can retain their morphological stability over the cycles [10–13]. However, it turned out that the morphological stability is a necessary but not sufficient condition to have electrodes with cycling stability, satisfactory for commercialization. It was revealed that the carbonaceous phase plays an important role in improving the cycle performance of the mixed Si/C composites.

This study is focused on additional reasons that might be significant; that is the type of the current collector, the type of the carbonaceous phase and the microstructure of the composite anode.

Fig. 1 shows the cycle test of mixed Si:MCMB (1:1) composite pasted on both nickel foam and copper foil current collectors. As seen in the figure, there is no considerable difference between both cases except for the slightly different irreversible capacity loss during the initial cycles. Although such a high irreversible capacity loss cannot be accepted in practical LIB, it is notable that after the first few cycles further cycling proceeds with high coulombic efficiency, comparable with the values typical for the carbonaceous hosts. Irreversible capacity loss over the initial cycles was found to be proportional to the BET surface area of the Si/C composite. Since composites used in this work have BET surface area in the order of $20 \, m^2 \, g^{-1}$, their reversibility during the initial cycle is ca. 60%. This can be seen in the voltage profile of the composite pasted on a copper current collector shown in Fig. 2.
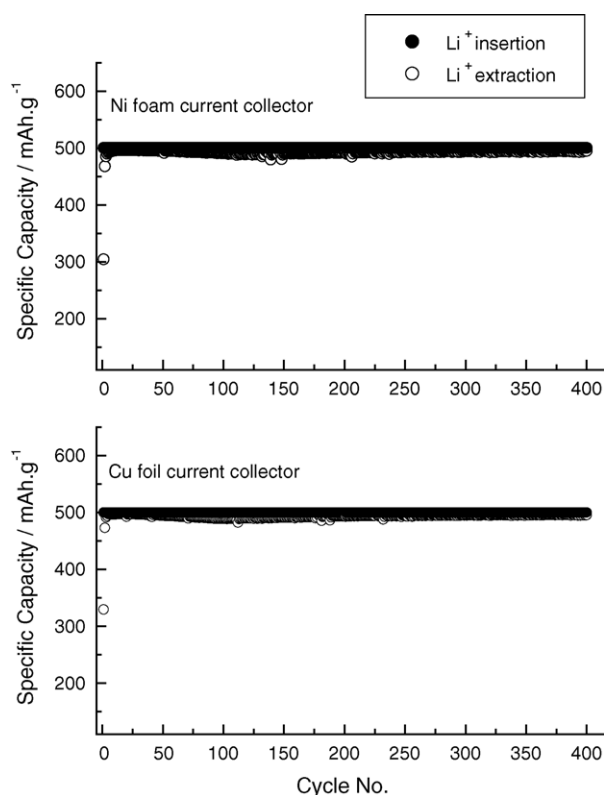

Fig. 1. Cycle performance of *p*-Si:MCMB (1:1) pasted on both nickel foam and copper foil current collectors.
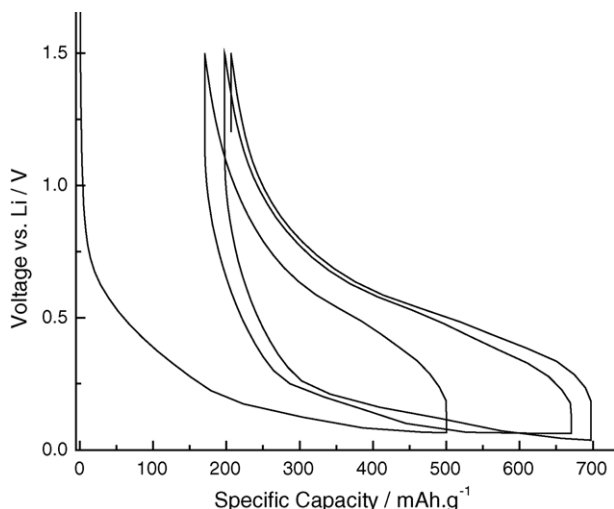
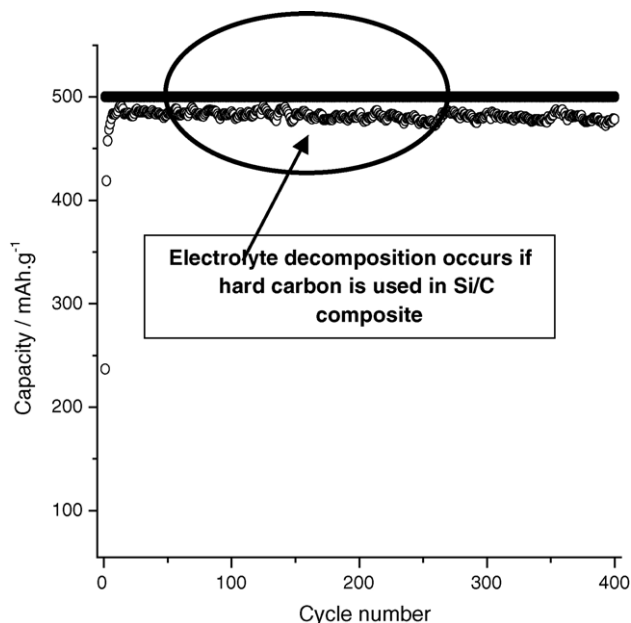Fig. 2. Voltage profile of *p*-Si:MCMB (1:1) material pasted on a copper foil current collector.

Fig. 3. Cycle performance of *p*-Si (1 μm):T4B2 (1:1). Note the large irreversibility of this electrode despite the large cycle number.
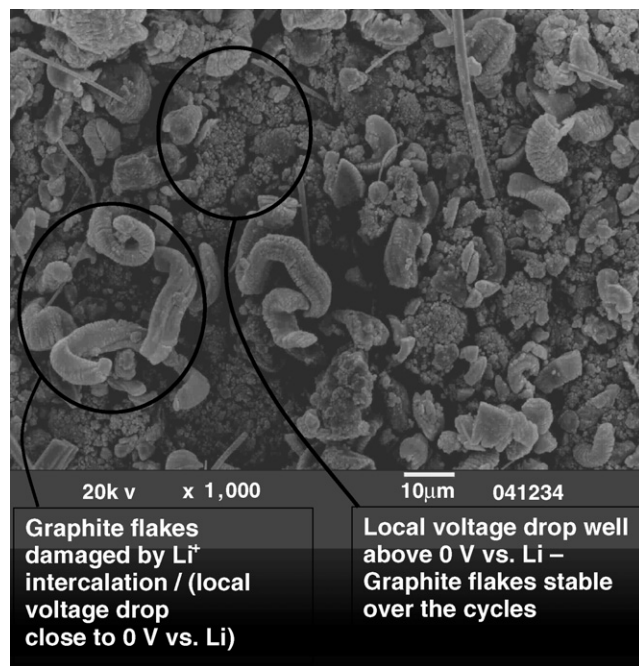

Fig. 5. SEM image of a graphite electrode cycled in 1 M LiPF$_6$ dissolved in PC/EMC 1:5. PC in such a concentration can be used as a fingerprint for graphite flakes exfoliation, which is favored when the local voltage drop is close to 0 V vs. Li.

Fig. 3 shows cycle test for composite Si:hard carbon (T4B2). One can see that the coulombic efficiency does not reach values comparable with those for the pure carbonaceous hosts. Thus, despite there is no deep intercalation into graphite the cycling cannot proceed with high efficiency, probably due to continuous electrolyte decomposition of the electrolyte on the surface of the hard carbon particles, present in the composite.

This effect can be understood quantitatively if considering in detail the structure of the Si/C composite electrode, which is schematically shown in Fig. 4. During the cycling test one always deals with the average value of the electrode potential, practically recorded as a voltage profile. However, the electrode possesses a micro-heterogeneous structure, although this heterogeneity is not easily measurable because of the small size
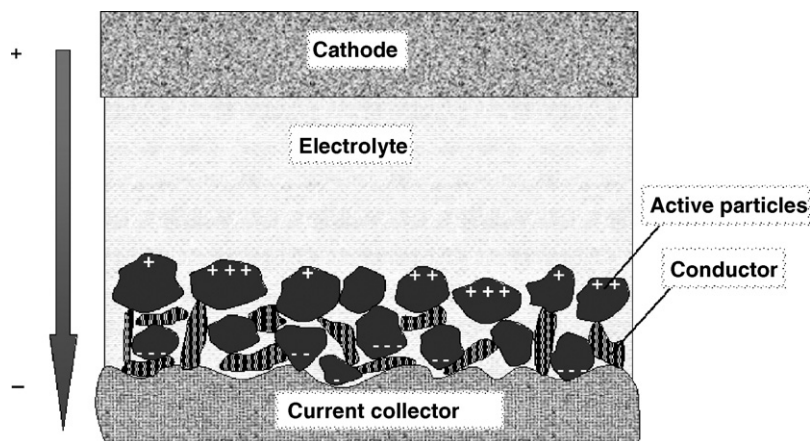

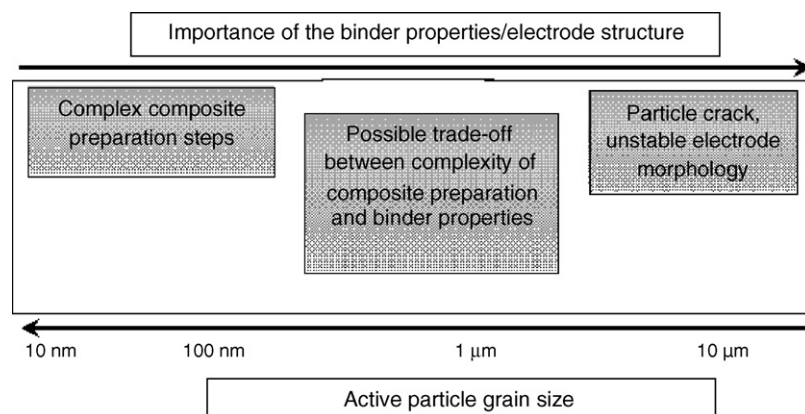Fig. 4. Sketch of the composite Si/C electrode.

Fig. 6. Schematic explanation of the possible drawback between complexity of the silicon-based composite preparation and practical scalability.

of the micro-heterogeneous domains. An evidence for such a heterogeneous structure is presented in Fig. 5, which shows surface of a graphite electrode cycled in 1 M LiPF$_6$ dissolved in PC/EMC 1/4 by volume. PC in such a low concentration serves as a fingerprint for graphite exfoliation. It is seen that there are different regions shown in the picture. Within some of them graphite flakes are damaged by PC co-intercalation, favored by a local voltage drop close to 0 V versus Li. On the contrary, there are other regions where graphite flakes remain stable since local voltage drop is well above 0 V versus Li. Local voltage drops are an indication of local electrode structure fluctuations. The appearance of such local fluctuations is very sensitive to the amount of the conductive additives, binder properties and electrode fabrication conditions. Particularly in the case of Si/C mixed composites, the silicon particles grain size plays a crucial role for the local electrode structure fluctuations. The latter are very large when the particle grain size of the initial silicon powder present in the composite exceeds 2–3 μm. This is the reason why to use Si powder with grain size in the order of 1 μm or less. Quantification of all aforementioned effects is not an easy task and special and careful optimization is necessary in order to fabricate an electrode with satisfactory performance.

Although this work sheds light on effects which have not been previously investigated, one should bear in mind all effects so far revealed in the literature regarding composite silicon-based anodes for LIB. It is expected that a trade-off between complexity of preparation and practical scalability of silicon-based composite anodes may be achieved as shown in Fig. 6. Smaller particle grain sizes generally lead to more uniform electrode structure at the expense of complex preparation steps. For the time being, there is no practical method of preparing sufficient amounts of Si-nanopowder with the desired properties (left region of the down arrow). Contrary to that, large particles which are easily obtained do not provide stable electrode morphology/texture (right region of the down arrow). A possible trade-off is shown in the middle region: particles with grain sizes within 0.5–1.0 μm. Such powders can be obtained comparatively easy in large amount and at the same time they allow the preparation of morphologically stable electrodes.

4. Conclusions

This work continues our study on mixed Si/C composite materials for LIB. Fixed capacity testing method, which allows working at strictly defined conditions was employed. Additional finding is that the composite electrode may possess a micro-heterogeneous structure. Local voltage drops close to 0 V may lead to deposition of metallic Li or destruction of the carbonaceous phase. A fingerprint of this process is electrolyte containing small amount of PC, whose co-intercalation is favored by local voltage drops close to 0 V. Heterogeneous structure of such an electrode is an indirect evidence of such a mechanism.

Acknowledgement

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